LIBRARY
Brigham Young University

COLLECTION ON GEOLOGY AND ENGINEERING

FROM DR. ALBERT CLARENCE BOYLE, JR.

CALL NO. [redacted]

ACC. NO. [redacted]

G. Q. Coray

Ithaca

N. Y.

QD
71
.D68x

QUALITATIVE

CHEMICAL ANALYSIS.

A

GUIDE IN THE PRACTICAL STUDY OF CHEMISTRY

AND IN

THE WORK OF ANALYSIS.

158677

BY

SILAS H. DOUGLAS, M.A., M.D.,

AND BY

ALBERT B. PRESCOTT, M.D., F.C.S.,

AUTHOR OF "OUTLINES OF PROXIMATE ORGANIC ANALYSIS," "CHEMICAL EXAMINATION OF ALCCHOLIC LIQUORS," AND "FIRST BOOK OF QUALITATIVE CHEMISTRY."

B.Y.U.
LIBRARY
PROVO, UTAH

FOURTH EDITION, WHOLLY REVISED.

WITH

A STUDY OF OXIDATION AND REDUCTION.

BY OTIS COE JOHNSON, M.A.

NEW YORK:
D. VAN NOSTRAND, PUBLISHER,
23 MURRAY STREET AND 27 WARREN STREET.
1883.

Entered according to Act of Congress, in the year 1880, by

D. VAN NOSTRAND,

In the Office of the Librarian of Congress, at Washington.

U.S.G.
WARD
HAT.OVOM

H. J. HEWITT, PRINTER, 27 ROSE STREET, NEW YORK.

PREFACE TO THE FIRST EDITION.

THE first edition of Douglas' *Tables for Qualitative Analysis* was published in 1864, the second edition in 1865, and the third in 1868. That work was prepared to be used with Fresenius' *Manual of Qualitative Analysis*, and was designed, firstly, as a graphic outline to accompany the larger text-book, and, secondly, as *a guide in the experimental study of substances*—to be made in connection with analysis, but beyond its immediate requirements. In this manner the work has been used by the authors, with the students in the chemical laboratory of this University, for the past ten years.

Notwithstanding the pre-eminent value of the manuals of Fresenius as standard authority in analysis, and the worth of other books extant for their several purposes, it now seems desirable to use a work more fully to serve for instruction in what might be termed comparative chemistry; and likewise to relieve the student from the immediate necessity of obtaining more than one text-book for inorganic qualitative work.

To aid the student in gaining an accurate acquaintance with the facts whereby analyses are made, and a clear understanding of the co-ordination of these facts—the principles of analysis—has been the chief object in this work. It is the result of experience in the constant endeavor to prevent habits of automatic operation and of superficial observation in analysis.

Further, it is desired that the book may be found convenient and reliable for reference by chemists, pharmacists, and others, who occasionally or habitually perform analyses.

The organic bases and acids, with a few exceptions, have been omitted from consideration. This is not done from neglect, but from a conviction of their too great importance for the subordinate and cursory attention which can be given to them in works devoted mainly to inorganic analysis.

To the faithful workers who have wrought out the great science of Chemistry, the writers humbly acknowledge their indebtedness for whatever of truth or value this little manual may contain.

UNIVERSITY OF MICHIGAN, September, 1873.

PREFACE TO THE SECOND EDITION.

In this edition, tabular summaries of the comparative reactions of groups of bases and acids have been introduced, as a means of training the beginner in the Principles of Analysis. They can be used in first practice, with known material, before undertaking systematic analysis ; and they also serve as indexes for practice in synthetic reactions to follow separative work. The authors have, for some time, employed summaries of this kind in class-teaching of laboratory students, and believe their incorporation with the text will be found helpful.

For the analysis of the "Third Group," in absence of phosphates, plans are tabulated both with and without the division by ammonium hydrate and chloride; and two plans are tabulated for the work in presence of phosphates. Additional reactions have been introduced throughout, and the rare elements presented, with a constant endeavor to respect the limits of a compact manual; to which end, the text not required by the beginner has been put in smaller type. The transitional use of barred symbol-letters in notation has been discontinued, and the nomenclature made uniform.

Our acknowledgments are due to Professor Wm. Ripley Nichols, of the Massachusetts Institute of Technology; Professor W. O. Semans, of Delaware, Ohio; and others—for suggestions in the choice of processes. Thanks are especially due to Mr. Otis C. Johnson, since 1871 an Instructor in Qualitative Analysis at Michigan University, for improvements in details of analysis, and for certain results of his unfinished investigations upon oxidation and reduction.

University of Michigan, October, 1876.

PREFACE TO THE THIRD EDITION.

THE text upon Oxidation and Reduction, by Mr. Johnson, is presented, as Part IV., in this edition, with much interest as to the reception which its distinctive method may obtain among chemists. If it were given only as a compend of the chief inorganic changes of oxidation, it could be commended without hesitation, for instruction in a field of unequalled value to the student of qualitative chemistry. All the reactions have been confirmed by the author, some of them have been first established by him, and the most of them have been verified by his students, for the past six or eight years. But as Mr. Johnson's compend is given with a new interpretation of quantivalence, adopting a provisional function of this term, it is submitted with some uncertainty as to what may be thought of it. As a teaching method we can testify to the marked success of the proposed rendering of quantivalence, in elucidating and classifying the reactions of oxidation, and in balancing equations. Aside from any applications of molecular physics, or any question of constructing molecules, *the bond* is used only as the index of active chemism—representing at least one function of active or apparent quantivalence. As chemism acts between unlike particles—positive and negative factors—so bonds are stated as being *either positive or negative bonds.* Mr. Johnson takes leave to borrow the bond, as a known character in quantivalence, and to use it in carrying out his special study of oxidation. Possibly it may appear that the adoption of another term will be open to less objection than the addition of another definition for the established term.

This edition has been diligently revised throughout, and though not trusting to have escaped all besetting errors, the authors hope, now, better to deserve the favor which has been granted to this work, for all which they desire to present grateful acknowledgments.

UNIVERSITY OF MICHIGAN, June, 1880.

CONTENTS.

PAGE

INTRODUCTORY:

The Notation of Metallic Compounds 9
Table of Atomic Weights and Quantivalence 13
The Study of Chemical Analysis 15

PART I. THE METALS:

Classification of the Metals 27

GROUP V.: *The Alkali Metals* 29
Potassium 31
Sodium 32
Ammonium 33
Lithium 35
Rubidium and Cæsium 36

GROUP IV.: *The Alkaline Earth Metals* 37
Barium 38
Strontium 40
Calcium 40
Magnesium 42
Comparative Reactions of the Metals of the Alkaline Earths 44
Separation of the Fourth Group Metals 45
Separation of Magnesium from the Alkali Metals 46

GROUP III.: *The Metals of the Earths and the more Electro-positive of the Heavy Metals* 46
Aluminium 49
Chromium as a Base 51
Chromic Acid 53
Iron 54
Manganese 60
Manganous Salts 61
Cobalt 63
Nickel 66
Zinc 68
Comparison of Reactions of Third Group Bases 71
Separation by Ammonium Hydrate, etc., Table 72
Separation by Thiosulphate Process 74
Separations of the Metals of the Third Group 75
Separation of Phosphates, with Alkali Acetate, Table 78
Cerium, Beryllium, Uranium, Titanium, Thallium 80
Comparative View of the Ten remaining Rare Metals of Group III 84

PAGE

GROUP II.: *Metals whose Sulphides are Insoluble in Dilute Acids* 85
Copper 87
Bismuth 91
Cadmium 94
Comparison of Bismuth, Copper, and Cadmium 95
Lead 95
Silver 100
Mercury 104
Mercurous Salts 105
Mercuric Salts 109
Comparison of First Group Metals 111
Arsenic 112
Antimony 123
Tin 130
Comparison of Arsenic, Antimony, and Tin 135
Separation of the Metals of the First and Second Groups 136
Methods for separating the Bases without the use of Sulphides 145
Gold 148
Platinum 149
Palladium 152
Molybdenum 153
Ruthenium, Iridium, Rhodium, Osmium 156
Telurium, Selenium, Tungsten 156

PART II. THE NON-METALS AND THE ACIDS:

Chlorine 157
Hydrochloric Acid 158
Chloric Acid 160
Perchloric Acid 161
Hypochlorous Acid 162
Bromine 163
Hydrobromic Acid 163
Bromic Acid 165
Iodine 166
Hydriodic Acid 167
Iodic Acid 170
Comparative View of Reactions of the Acids of Chlorine, Bromine, Iodine 173
Separation of the Acids of Chlorine, Bromine, and Iodine 174
Nitrogen and the Nitrogen Group 175
Nitric Acid 176
Nitrous Acid 180
Cyanogen 181
Hydrocyanic Acid 181
Hydroferrocyanic Acid 184
Hydroferricyanic Acid 186
Cyanic Acid 188
Sulphocyanic Acid 188
Carbon 190
Carbonic Anhydride 191
Oxalic Acid 193

PAGE
Sulphur ... 194
Hydrosulphuric Acid ... 195
Sulphuric Acid ... 197
Sulphurous Acid ... 199
Comparison of Hydrosulphuric, Sulphurous, and Hydrocyanic Acids ... 202
Thiosulphuric Acid ... 203
Phosphorus ... 205
Phosphoric Acids ... 205
Orthophosphoric Acid ... 206
Pyrophosphoric Acid ... 208
Metaphosphoric Acid ... 208
Comparison of Sulphuric, Oxalic, and Phosphoric Acids ... 209
Hypophosphorous Acid ... 210
Boracic Acid ... 210
Silicic Acid ... 212
Fluorine ... 213
Hydrofluoric Acid ... 213
Hydrofluosilicic Acid ... 214
Acetic Acid ... 214
Tartaric Acid ... 215
Citric Acid ... 216

PART III. SYSTEMATIC EXAMINATIONS:

Separation of the Acids from the Bases and from each other ... 218
Conversion of Solids into Liquids ... 219
Separation from Organic Matter ... 220
Preliminary Examinations of Solids ... 222
Systematic Examinations in the Dry Way ... 227
Tests in Beads of Borax and Phosphorus Salt ... 235
Analysis for the Metals, Tables ... 236
Analysis for the Acid Radicals, Tables ... 244

PART IV. OXIDATIONS ... 250

APPENDIX.

Solubilities of Salts: I. In Reference to Bases ... 284
II. In Reference to Acids ... 292
General Table of Solubilities ... 295
Reagents Used in Analysis ... 296

THE NOTATION OF METALLIC COMPOUNDS.

ACIDS. An acid is a salt of hydrogen. It consists of an *Acid Radical*,* united with hydrogen which can be exchanged for a metal, this being the formation of a salt. The hydrogen is the base of the acid; as the metal is the base of the salt. Sulphuric acid, for instance, is sometimes written hydrogen sulphate. *Oxacids* are those whose radicals contain oxygen, as HNO_3. *Hydracids* are those whose radicals have no oxygen, as HCl; their names begin with *hydr* and end with *ic*, and the names of their salts end in *ide*. The *Anhydride* of an oxacid is what remains after removing from the acid its basic H,† and enough O to form H_2O with the H. Thus, the anhydride of H_2SO_4 is SO_3, and carbonic anhydride is CO_2, carbonic acid being H_2CO_3. Acids whose molecules contain but one atom of basic hydrogen are termed *monobasic*, as HNO_3 and HCl; those with two atoms of hydrogen in the molecule, *dibasic;* as H_2SO_4 and H_2S; those with three hydrogen atoms, tribasic, as H_3PO_4; etc. Some of the more important acids are given in the following list:

HCl,	hydrochloric	acid or hydrogen		chloride.
$HClO_3$,	chloric	"	"	chlorate.
HBr,	hydrobromic	"	"	bromide.
$HBrO_3$,	bromic	"	"	bromate.
HI,	hydriodic	"	"	iodide.
HIO_3,	iodic	"	"	iodate.
HNO_3,	nitric	"	"	nitrate.
H_2S,	hydrosulphuric	"	"	sulphide.
H_2SO_4,	sulphuric	"	"	sulphate.
H_2SO_3,	sulphurous‡	"	"	sulphite.‡
H_2CO_3,	carbonic	"	"	carbonate.
H_2CrO_4,	chromic	"	"	chromate.
H_3PO_4,	phosphoric	"	"	phosphate.

* A Radical is a group of atoms, or a single atom, which retains its integrity while transferred from one molecule to another, being a leading constituent of each.

† The organic acids mostly contain H in the radical, and not exchangeable for a metal—that is, not basic hydrogen, as $H(C_2H_3O_2)$.

‡ Oxacids whose names end in *ic* form salts with names ending in *ate;* while those, containing less oxygen, whose names end in *ous* make salts having names ending in *ite*.

H_3AsO_4,	arsenic	acid or hydrogen		arseniate.
H_3AsO_3,	arsenious	"	"	arsenite.
H_3FeCy_6,	hydroferricyanic	acid	"	ferricyanide.
H_4FeCy_6,	hydroferrocyanic	"	"	ferrocyanide.
$HC_2H_3O_2$,	acetic	"	"	acetate.
$H_2C_2O_4$,	oxalic	"	"	oxalate.

SALTS. A salt is formed by substituting a metal for the hydrogen of an acid, each bond* of the metal displacing one atom of hydrogen. As follows:

K′	with	HNO_3	forms	KNO_3,	displacing	H
K'_2	"	H_2SO_4	"	K_2SO_4,	"	2H
K'_3	"	H_3PO_4	"	K_3PO_4,	"	3H
Ca″	"	H_2SO_4	"	$CaSO_4$,	"	2H
Ca″	"	$2HNO_3$†	"	$Ca(NO_3)_2$,	"	2H
Bi‴	"	$3HNO_3$	"	$Bi(NO_3)_3$,	"	3H
3Ca″	"	$2H_3PO_4$‡	"	$Ca_3(PO_4)_2$,	"	6H
2Bi‴	"	$3H_2SO_4$	"	$Bi_2(SO_4)_3$,	"	6H

A *normal salt* is formed (like those above given) by displacing all the hydrogen of the acid with an equivalent of metal. An *acid salt* is formed by exchanging a part of the hydrogen of an acid for an equivalent of metal. Thus:

K′	with	H_2SO_4	may form	$KHSO_4$,	an acid sulphate.
K′	"	H_3PO_4	"	KH_2PO_4	" phosphate.
2K′	"	H_3PO_4	"	K_2HPO_4	" "
Ca″	"	H_3PO_4	"	$CaHPO_4$	" "
Ca″	"	$2H_3PO_4$	"	$CaH_4(PO_4)_2$	" "

A *basic salt* is formed by the substitution of a metal in part for the hydrogen of an acid and in part for the half or the whole of the hydrogen of water (H_2O). For example:

Bi‴ with $\left\{\begin{matrix}HNO_3\\H_2O\end{matrix}\right.$ forms Bi $\left\{\begin{matrix}NO_3\\O\end{matrix}\right.$, a basic nitrate, usually written $BiONO_3$.

Again, $Pb''_3(OH)_2(CO_3)_2$ is a basic carbonate of lead. A basic salt is partly of the nature of a salt and partly of the nature of a hydrate or oxide.

HYDRATES AND OXIDES of Metals. A metallic hydrate is formed by substituting a metal for half the hydrogen of water (H_2O), bond for bond.

* The number of *bonds* of any element (or radical) is an expression of its capacity for chemical combination, the combining capacity of one atom of hydrogen being the unit. The number of bonds, or *the quantivalence*, is denoted by the common names, monad, dyad, triad, tetrad, etc.; also by the qualifying terms, univalent, bivalent, etc., and, in notation, by indices, thus, H′, O″, N‴, etc.

$$\dagger\ Ca + \left\{\begin{matrix}HNO_3\\HNO_3\end{matrix}\right. = Ca\left\{\begin{matrix}NO_3\\NO_3\end{matrix}\right. + \left\{\begin{matrix}H\\H\end{matrix}\right.$$

$$\ddagger\ \left.\begin{matrix}Ca\\Ca\\Ca\end{matrix}\right\} + \left.\begin{matrix}H_3PO_4\\H_3PO_4\end{matrix}\right\} = \left.\begin{matrix}CaPO_4\\Ca\\CaPO_4\end{matrix}\right\} + \left.\begin{matrix}HH\\HH\\HH\end{matrix}\right\}$$

Na'	with	H_2O	forms	$NaOH$,	sodium hydrate.
Ba''	"	$2H_2O$	"	$Ba(OH)_2$,	barium "
Fe_2^{VI}	"	$6H_2O$	"	$Fe_2(OH)_6$,	ferric "

The **OH**, which, as a fragment of the water-molecule, unites with metals, is known as hydroxyl—a monad radical. The term *hydroxide* has been introduced by some chemists, instead of hydrate, for the compounds of hydroxyl.

A metallic *oxide* is formed by substituting a metal for all the hydrogen of water, bond for bond. Mg'' with H_2O forms **MgO**, displacing 2H. An oxide, then, is simply a union with oxygen (O'').

In recapitulation, then, *the number of bonds of the metal* equals

The number of bonds of acid radicals, in *normal salts;*
" " hydroxyl, in *hydrates;*
" " oxygen, in *oxides.*

In *acid salts*, the remaining atoms of **H** are counted with the bonds of metal; in *basic salts*, the bonds of **(OH)** and of **O** are counted with the bonds of acid radical.

The more important **BASES** are given in this list:

K'	the base of	potassium	or	potassic	salts.
Na'	"	sodium	"	sodic	"
NH_4'	"	ammonium	"	ammonic	"
Ag'	"	silver	"	argentic	"
Ba''	"	barium	"	baric	"
Sr''	"	strontium	"	strontic	"
Ca''	"	calcium	"	calcic	"
Mg''	"	magnesium	"	magnesic	"
Zn''	"	zinc	"	zincic	"
Ni''	"	nickel	"	nickelous	"
Pb''	"	lead	"	plumbic	"
Hg''	"	. . . . .		mercuric	"
Hg_2''	"	. . . . .		mercurous	"
Cu''	"	copper	"	cupric	"
Cu_2''	"	. . . . .		cuprous	"
Fe''	"	. . . . .		ferrous	"
Fe_2^{VI}†	"	. . . . .		ferric	"

* As in mercurous chloride: $\begin{matrix} Hg-Cl \\ | \\ Hg-Cl \end{matrix}$

† In the *pseudo-triads* or "double triads" (**Fe, Mn, Co, Cr, Al**) an even number of atoms is always found in the molecules, two atoms having six bonds. The atoms are supposed to be tetrads, one of the four bonds of each atom being held by a fellow-atom of the same element. Thus, in ferric compounds, we have $''Fe-Fe'''$; and, for ferric chloride, $\begin{matrix} Cl & Cl \\ Cl & Cl \end{matrix}\ Fe-Fe\ Cl$

Mn''	the base of	. . . . .	manganous salts.
Mn_2^{VI}	"	. . . . .	manganic "
Co''	"	. . . . .	cobaltous "
Co_2^{VI}	"	. . . . .	cobaltic "
Al_2^{VI}	"	aluminium or	aluminic "
Cr_2^{VI}	"	chromium "	chromic "
Bi'''	"	bismuth "	bismuthous "
Sn''	"	. . . . .	stannous "
Sn''''	"	. . . . .	stannic "
Sb'''	"	. . . . .	antimonious "
Sb^V	found in	. . . . .	antimonic compounds.
As'''	"	. . . . .	arsenious "
As^V	"	. . . . .	arsenic "

TABLE OF ATOMIC WEIGHTS[1]

AND

QUANTIVALENCE.[2]

Aluminium,	Al'''''*	27.3
Antimony,	Sb''', v	122.0
Arsenic,	As''', v	74.9
Barium,	Ba''	136.8
Beryllium,	Be''	9.0
Bismuth,	Bi''', v	210.0
Boron,	B'''	11.0
Bromine,	Br', v	79.9
Cadmium,	Cd''	111.6
Cæsium,	Cs'	133.0
Calcium,	Ca''	39.9
Carbon,	C''''	12.0
Cerium,	Ce''', $''''$	141.3
Chlorine,	Cl', v	35.5
Chromium,	Cr''''*, vi	52.4
Cobalt,	Co'', $''''$*	58.6
Copper,	Cu''†	63.0
Davyum,		154.0
Decipium,	Dp	
Didymium,	D'''	145.0
Erbium,	E'''	169.0
Fluorine,	F'	19.1
Gallium,	G''''*	69.8
Gold,	Au', $'''$	196.2
Hydrogen,	H'	1.0
Ilmenium,	Il	104.0
Indium,	In''''*	113.4
Iodine,	I', v	126.8
Iridium,	Ir'', $''''$*, vi	196.7
Iron,	Fe'', $''''$*, vi	55.9
Lanthanum,	La'''	139.0
Lavoisium,		
Lead,	Pb'', $''''$	206.4
Lithium,	Li'	7.0
Magnesium,	Mg''	23.9
Manganese,	Mn'', $''''$*, vi	54.8
Mercury,	Hg''†	199.8
Molybdenum,	Mo'', $''''$*, vi	96.0
Mosandrum,		
Neptunium,	Np^{v}	118.0
Nickel,	Ni'', $''''$*	58.6
Niobium,	Nb^{v}	94.0
Nitrogen,	N''', v	14.0
Osmium,	Os'', $''''$*, vi	198.6
Oxygen,	O''	16.0
Palladium,	Pd'', $''''$	106.2
Philipium,	Pp	
Phosphorus,	P', $'''$, v	31.0
Platinum,	Pt'', $''''$	196.7
Potassium,	K'	39.0
Rhodium,	Ro'', $''''$*, vi	104.1
Rubidium,	Rb'	85.2
Ruthenium,	Ru'', $''''$*, vi	103.5
Selenium,	Se'', $''''$, vi	78.0
Silicon,	Si''''	28.0
Silver,	Ag'	107.7
Sodium,	Na'	23.0
Strontium,	Sr''	87.2
Sulphur,	S'', $''''$, vi	32.0
Tantalum,	Ta^{v}	182.0
Tellurium,	Te'', $''''$, vi	128.0
Thallium,	Tl',$'''$	203.6
Thorium,	Th''''	231.5
Tin,	Sn'', $''''$	117.8
Titanium,	Ti'', $''''$*	48.0
Tungsten,	W'''', vi	184.0
Uranium,	U'''', vi	240.0
Vanadium,	V''', v	51.2
Yttrium,	Y'''	93.0
Zinc,	Zn''	64.9
Zirconium,	Zr''''	90.0

[1] Decimals beyond the first place are omitted. Stas, an accepted authority, gives oxygen the atomic weight of 15.96; nitrogen, 14.009; sulphur, 31.98; etc.

[2] By quantivalence is here meant active or apparent quantivalence, in its principal degrees.

* Pseudo-triads, as Al_2^{vi}, Fe_2^{vi}, etc.

† In cuprous compounds, Cu_2''. In mercurous compounds, Hg_2''.

THE STUDY OF CHEMICAL ANALYSIS.

1. *Chemical Analysis is the determination of the composition of matter.* Any portion of matter—solid, liquid, or gaseous; amorphous, crystalline, or organized—consists of one or more distinct substances. A distinct substance is made up of molecules* which are exactly alike. It is a discrete kind of matter, invariably the same in every quality; it may be a compound or an element. It will be borne in mind that, in chemistry, compounds are bodies unlike the elements that have formed them. Thus, we may have to analyze a mixture containing sodium sulphate (Na_2SO_4); sodium sulphite (Na_2SO_3), and sodium thiosulphate ($Na_2S_2O_3$); but not containing any sodium, or sulphur, or oxygen, as these bodies are known to the world. The complete analysis of a given portion of material reveals all the distinct substances by which it is made up. Also compounds are subjected to analysis to find from what component elements they have been formed. Hence, chemical analysis enables us to state the composition of matter in terms of the seventy elements.

2. An analysis may be **partial,** as in testing a mixture for presence of arsenic or for proportion of gold; or it may be **complete,** when all the constituents are to be found.

In **qualitative analysis,** it is ascertained what substances are present in the material; in **quantitative analysis,** their proportion by weight is determined.

When the material to be examined is in the gaseous state, its examination, qualitative or quantitative, is termed **Gas Analysis,** which is a distinct branch of analysis. The chemical examination of material consisting of the more complex compounds of carbon, whether qualitative or quantitative, is known as **Organic Analysis: Ultimate,** when the elements are determined; **Proximate,** when the constituent compounds are determined. In ultimate organic analysis, few elements require determination; the task is not difficult, and the art has been highly perfected. On the contrary, in proximate organic analysis, a great number of compounds have to be considered; identification is often difficult, and no comprehensive system has been completed. The term Qualitative

* A *molecule* is the smallest possible portion of a distinct substance. It exists free; its quality being independent of relations to other portions of matter. It cannot be divided, or chemically united to any other particles of matter, without the production of one or more new molecules and the occurrence of a change of properties.

An *atom* is an indivisible constituent of a molecule. It exists in combination; its quality being in part dependent upon its relations to the other constituents of its molecule. In the elementary substances, the molecules consist of like atoms; two atoms, in most cases, constituting a molecule.

Analysis, then, as it is commonly used, is limited to the chemical examination of solid and liquid material, chiefly of mineral origin.

3. In qualitative analysis of mixtures, it is often but not always necessary to *separate* substances in order to *identify* them; in quantitative analysis, their accurate separation is almost invariably required. Identification necessarily supposes comparison: in testing for a substance we consider what other substances can be present to simulate it; in separating a substance or a class of substances, we must know from what other substances or classes we remove it; to accomplish either task we must proceed in *systematic order* and conduct our operations, consecutively, in obedience to some intelligent method, based on a knowledge of the comparative properties of all the substances which may be present.

Both the identification and separation of substances are accomplished, nearly always, by inducing *changes*, chemical and physical. The *methods of analysis* are as numerous as are the ways of bringing into action physical and chemical agents for the induction of changes. A substance is characterized by its deportment under the influence of these agents—as its manifestation of cohesion, varied at different temperatures, its degree of adhesion for certain solvents, its color and other phenomena with light, and the results of its chemism when brought in contact with other substances technically called reagents. The results last named, those of chemical action, are the most important of the resources of analysis. By chemical change, a substance in the material under examination becomes resolved into other distinct substances, each capable of recognition by its own deportment and its own capacities for chemical transmutation, and each product adding evidence in the identification of the original substance.

4. The operations of analysis embrace those **in the dry way**, and those **in the wet way.**

In the dry way, substances are taken in the solid state, and are subjected to a high heat—over a lamp, before a blow-pipe, or in a furnace—generally with solid reagents, which enable the mass to melt, or abstract oxygen, or supply oxygen. *The liquid state*, whether produced in fusing at a red or white heat, or by solution in some solvent at ordinary temperatures, is the state generally essential to chemical change. Analysis in the dry way resembles the **metallurgic** operations by which most commercial metals are obtained from their ores; it may be made quantitative, as in the process of **assaying** of the precious metals, in use since ancient times; it is limited to *partial* analysis, not enabling us to determine all constituents of unknown mixtures; it is seldom exclusively employed, except in **determinative mineralogy,** or finding the species of minerals, and in **assaying**; it is used in full qualitative analysis as a **preliminary examination,** subordinate to that in the wet way, and some of its operations are indispensable, in connection with the wet methods, for certain substances. The details of manipulations in the dry way are described

in connection with each substance to which they are applicable, and under Preliminary Examination of Solids.

5. **Spectroscopic Analysis,** and the inspection of incandescent vapors, either directly or through colored media, furnish important resources for identifying substances, quite distinct from the operations of chemical analysis, but associated with them in practice.

6. The operations in the wet way constitute much the most extensive means of analysis, also the most frequent mode of synthesis, and by far the most instructive field of chemical experiment. For these operations the material, if not already liquid, is first brought into *the liquid state,* not by fusion but by solution. It is treated with reagents in the liquid state; and substances are identified and separated mostly by changes which return them from the liquid to the solid, or, less often, to the gaseous state. It is evidently necessary, therefore, in the beginning to understand clearly the precise nature of the simple occurrences of *solution, precipitation,* and *vaporization.*

7. Solution is the liquefaction of a solid, or a gas, by mixture with a liquid. The term is also sometimes applied to the mixture of two liquids: as glycerine is soluble (miscible) in alcohol, but insoluble (not miscible) in ether. The mixture is effected by *adhesion,* an elective union in indefinite proportions, and not forming a new substance. If a solid dissolves in a liquid, the adhesion between the two substances is sufficient to overcome the *cohesion* that preserved the solid. There is adhesion between sponge and water, not sufficient to overcome the cohesion of the sponge; and between sugar and ether, not sufficient to overpower the cohesion of the sugar; but between sugar and water, exceeding the cohesive force of the sugar, and it dissolves. If a gas dissolves in a liquid, adhesive force proves stronger than the elasticity of the gas.

8. The most universal solvent is water; it is always understood to be present, in indefinite proportion, in operations in the wet way; it serves as a vehicle, as such not being included in any statement of the substances operated upon, any more than is the material of the test-tube, but often some portion of it enters into combination or suffers decomposition, and then it must be placed among the substances engaged in the operation. Other solvents are: alcohol, either mixed with some water or anhydrous; ether, seldom quite free from mixture of alcohol; disulphide of carbon; benzene; glycerine, nearly or quite anhydrous; and others, less important.

9. No other property of substances has so great importance in analysis, and in all chemical operations, as their solubility in water. It must never be forgotten that there are *degrees* of solubility, but there is hardly such a fact as absolute solubility, or insolubility, regardless of proportion of the solvent. There are *liquids* which are miscible with each other in all proportions; but *solids* do not dissolve in all proportions of the solvent, neither do gases. For every solid, or gas, there is a least quantity of any solvent which can dissolve it. One part of potassium hydrate is soluble in one-half part of water (or in

any greater quantity), but not in a less quantity of the solvent. One part of sodium chloride requires at least two and a half parts of water to dissolve it. One part of mercuric chloride will dissolve in two parts of water at 100° C., but when cooled to 15° C., so much of the salt solidifies that it needs twelve parts more of water at the latter temperature to keep a perfect solution. Chloride of lead dissolves in about twenty parts of hot water, about half of the solid separating from the solution when cold. Sulphate of calcium dissolves in about 400 times its weight of water—this dilute solution forming one of the ordinary reagents. Sulphate of barium is said to dissolve in 200,000 parts of water; so that it is practically insoluble, one of the least soluble compounds known. Sulphate of lead dissolves in 13,000 parts of water; in most operations this solubility may be disregarded, but in quantitative analysis it is washed with alcohol instead of water, losing less weight with the former solvent. These examples indicate the necessity of discriminating between degrees of solubility.

10. The ordinary LIQUID REAGENTS are solutions in water—sulphuric acid and carbon disulphide being exceptions. Alcohol is usually mixed with a little water. (See the list of Reagents.) Hydrochloric acid, ammonia, and hydrosulphuric acid are aqueous solutions of *gases;* on exposure to air these gases gradually separate from their solutions, most rapidly in the case of hydrosulphuric acid solution; this gas having so little adhesion for water, and so great elasticity, that it will form only a dilute solution. All these gases escape much more rapidly when their solutions are warmed, being accompanied with some vapor of water. Sulphuric, nitric, and acetic acids are *liquid* when absolute; the latter two are instable when pure and are in mixture with water, in the authorized proportion, for use. The other ordinary liquid reagents are *solids* in aqueous solution.

11. Substances are said to dissolve in acids, or in alkalies, and this is termed **chemical solution:** more definitely it is chemical action *and* solution, the solution being always a merely physical change. We say that lime dissolves (chemically) in hydrochloric acid; that is, in the reagent named hydrochloric acid, and which is a mixture of that acid and water. The acid unites with the lime, forming a soluble solid, which the water dissolves. Absolute hydrochloric acid cannot dissolve lime.

12. Solids can be obtained, without chemical change, from their aqueous solutions, *firstly,* by **evaporation** of the water. This is done by a careful application of heat, diminished at the close. In case volatile solids are in solution, such as ammonium salts and ferric chloride, a temperature much above that of boiling water will vaporize the solids, and of course a continuation of direct heat, after the water has all vaporized and latent heat ceases to be absorbed, will rapidly raise the temperature in the residue.

Solids can be removed from solution, without chemical change, *secondly,* by (physical) **precipitation**—accomplished by modifying the solvent. If solu-

tion of potassium carbonate, or of ferrous sulphate, be dropped into alcohol, a precipitate is obtained, because the salts will not dissolve or remain dissolved in the mixture of alcohol and water. But, in analysis, precipitation is generally affected by changing the dissolved substance, instead of the solvent.

Solids can be separated from their solution by **precipitation** due to *chemical change*, to the extent that the product is insoluble in the quantity of solvent present (observe 9). Calcium can be in part precipitated from not too dilute solutions of its salts, by addition of sulphuric acid; but there still remains not precipitated the amount of sulphate of calcium soluble, $\frac{1}{400}$ of the solution, which is enough to give an abundant precipitate with ammonium oxalate, the first precipitate being previously filtered out.

13. *Time is required* for the completion of most precipitates. If it is necessary to *remove* a substance, by precipitation, before testing for another substance, the mixture should stand, from several minutes to half an hour, before filtration. Neglect of this precaution often occasions a double failure; the true indication is lost, and a false indication is obtained.

14. *Reagents should be added in very small portions*, generally drop by drop. Often the first drop is enough. Sometimes a precipitate redissolves in the reagent that produced it, and this is ascertained if the reagent be added in small portions, with observation of the result of each addition. If it is a final test, a quantity of precipitate which is clearly visible, is sufficient; but if the precipitate is to be filtered out and dissolved, a considerable quantity should be formed. If the precipitate is to be removed and the filtrate tested further, the precipitation must be *completed*—by adding the reagent as long as the precipitate increases, with the warmth and time requisite in the operation; and a drop of the same reagent should be added to the filtrate to obtain assurance that the precipitation has been completed. It will be found, with a little experience, that some reagents must be used in relatively large quantities: this is especially the case with hydrosulphuric acid solution. The other acids —especially concentrated sulphuric, hydrochloric, and nitric—are required *in quantities relatively very small.*

15. *Precipitates are removed*—usually by filtration, sometimes by decantation. If they are to be dissolved, they must be first *washed till free from all the substances in solution.* If the precipitate has been made complete, there must be some excess of the reagent in solution, even in the closest work, and, if it is not required that the precipitate should be complete, excess of the reagent may have been used. Other substances are in solution, after a precipitation, as may be seen by a glance at the equation for the change. In an analysis of a complex mixture, there are substances in solution which are not chemically disturbed by one precipitation. All these dissolved substances permeate and *adhere* to the porous precipitate with greater or less tenacity. If they are not wholly washed away, some portion of them will be mixed with the dissolved precipitate. Then, the separation of substances, the only object

of the precipitation, is not accomplished, while the operator, proceeding just as though it was accomplished, undertakes to identify the members of a group by reactions on a mixture of groups. In such a case, the student is fortunate if the conflict between the "confirmatory reactions" and his supposed results becomes sufficiently evident to induce him to clean the test-tubes and commence the work at the beginning again—otherwise an incorrect result is reported. The washing, on the filter, is best completed by repeated additions of *small* portions of water—around the filter border, from the wash-bottle—allowing each portion to pass through before another is added. *The washings should be tested*, from time to time, until they are free from dissolved substances.

16. *In dissolving precipitates*—by aid of acids or other agents—*use the least possible excess of the solvent.* Endeavor to obtain a solution nearly or quite saturated, chemically. If a large excess of acid is carried into the solution to be operated upon, usually it has to be neutralized, and the solution is liable to become so greatly encumbered by additions of reagents and the water of their solution, that reactions become faint or inappreciable. Precipitates may be dissolved *on the filter*, without excess of solvent, by passing the same portion of the (diluted) solvent repeatedly through the filter, following it once or twice with a few drops of water. The mineral acids should be diluted to the extent required in each case; for solution of small quantities of carbonates and some other easily soluble precipitates, the acids may be diluted with fifty times their weight of water. Washed precipitates may also be dissolved *in the test-tube*, by rinsing them from the filter, through a puncture made in its point, with a very little water. If the filter be wetted before filtration, the precipitate will not often adhere to it very closely.

17. In adding an acid, or an alkali, to **saturation**, or **supersaturation**, or short of saturation, as may be directed, add by small portions, and after each addition shake and test upon a slip of litmus-paper, by a drop from a glass rod.

18. *Chemical Changes, as they occur in analytical operations, may be chiefly classified as follows:*

(1) Those of *Combination*, or synthesis, as when carbonic anhydride is formed by burning charcoal in the air, or when the vapors of ammonia and hydrochloric acid are brought together in the formation of ammonium chloride:

$$C^* + 2O = CO_2$$
$$NH_3 + HCl = NH_4Cl$$

* As the atoms of elements are united with each other in pairs, it is not philosophically correct to take an uneven number of atoms of any element in an equation. In this case, it must be explained, that the atom of carbon indicated in the equation was not found free, but was taken from a fellow-atom of carbon, which likewise combined with two atoms of oxygen. Hence the equation in the text represents the half of the smallest portions of matter that could engage in the operation. To avoid complexity in this work, equations will usually represent elements by atoms instead of molecules, and uneven numbers of atoms will be stated, wherever this is necessary to the lowest atomic terms of the equation.

(2) Those of *Dissociation*, or analysis in its limited sense, as in the production of oxygen and mercury by heating mercuric oxide, or of quicklime and carbonic anhydride by heating calcium carbonate:

$$HgO = Hg + O$$
$$CaCO_3 = CaO + CO_2$$

(3) Those of *Transposition*, or mutual replacement, as in the formation of plumbic sulphate and ferrous nitrate from solutions of plumbic nitrate and ferrous sulphate, or of zinc chloride and hydrogen from hydrogen chloride and zinc:

$$Pb(NO_3)_2 + FeSO_4 = PbSO_4 + Fe(NO_3)_2$$
$$2HCl + Zn = ZnCl_2 + 2H$$

(4) Those of *Oxidation and Reduction*, or change of active quantivalence, as in the production of stannic and mercurous salts from stannous and mercuric salts, or in the formation of sulphuric acid and arsenious oxide from sulphurous acid and arsenic oxide:

$$Sn''Cl_2 + 2Hg''Cl_2 = Sn''''Cl_4 + Hg_2''Cl_2$$
$$2H_2S''''O_3 + As^{V}{}_2O_5 = 2H_2S^{VI}O_4 + As'''{}_2O_3$$

19. When substances in separate solutions are brought together, one of the clearest evidences of the formation of new substances is the appearance of a solid or a gas in the mixture.

In most *cases of transposition or metathesis* [18(3)] this *change of state* is the only evidence showing the fact and the exact extent of chemical change. A solid, that is to say, a precipitate, which separates, on mixing two or more solutions, can be removed, and its quantity ascertained (12 and 15). A gas which separates from mixed solutions can be recognized by its properties, and sometimes by effervescence, and its quantity can be determined.

A change of transposition between dissolved substances—salts, acids, and bases—will take place when one or more of the products of such change is a solid, not soluble in the mixture:

(1) Transposition between two salts.

a. On mixing solutions of any two salts, capable of forming, by exchange of bases, a salt insoluble in the mixture—the insoluble salt is produced and precipitated:

potassic *sulphate* + *plumbic* acetate = *plumbic sulphate* + potassic acetate.

b. On mixing *solutions of two salts*, which, in transposition, form two new salts both soluble in the mixture—a partial exchange of bases takes place, and variable proportions of the two original salts and the two new salts remain in solution:

ferric chloride + potassic *sulphocyanate* = {ferric chloride. / *ferric sulphocy.*} + {potassic sulphocy. / potassic chloride.}

(2) Transposition between an acid and a salt.

a. On adding, *to a solution of a salt, an acid* which can form with the base

a salt insoluble in the solvent and in the produced acid—the insoluble salt is formed and precipitated:

argentic nitrate + hydric *chloride* = *argentic chloride* + hydric nitrate.

b. In adding, to a solution of a salt, an acid which can form with the base a salt insoluble in the solvent, but soluble in the produced acid (as diluted in the mixture)—no precipitate is formed:

ferrous sulphate + hydric sulphide = ferrous sulphate + hydric sulphide.

c. On adding to a solution of a salt (formed by a soluble acid), an acid which can form with the base a soluble salt—usually a partial exchange of acid radicals occurs, and variable proportions of two salts and two acids remain in solution:

potassic nitrate + hydric *sulphate* = { potassic nitrate / *potassic sulphate* } + { hydric sulphate. / hydric nitrate. }

d. On adding an acid to the solution of a salt the acid of which is insoluble in the solvent—the insoluble acid is formed and precipitated:

sodic *silicate* + carbonic acid = *silicic acid* + sodic carbonate.

(3) Transposition between an alkali and a salt.

a. The addition of a solution of a hydrate of *a base, to a solution of a salt*, the hydrate of the base of which is insoluble in the solvent present—causes a precipitate of the insoluble hydrate:

ferric chloride + ammonic *hydrate* = *ferric hydrate* + ammonic chloride.

b. The addition of a solution of a hydrate of a base, to a solution of a salt, the acid of which can form with the other base a salt insoluble in the solvent—causes a precipitate of the insoluble salt:

sodic *sulphate* + *baric* hydrate = *baric sulphate* + sodic hydrate.

c. The addition of a solution of a hydrate of a base, to a solution of a salt, the acid of which can form a soluble salt with the other base—usually causes a partial interchange of bases, leaving variable proportions of the two salts and two hydrates in solution:

sodic *chloride* + *potassic* hydrate = { sodic chloride / *potassic chloride* } + { potassic hydrate. / sodic hydrate. }

20. Transpositions in solution are determined *by forming the gaseous state*, as well as by forming the solid state. Generally, when, by decomposition between salts, acids and hydrates, both materials being in solution or one in solution and one solid—if there can be produced a substance *which is volatile* at the temperature of the operation—such substance is formed and vaporized. At ordinary temperatures:

calcic *carbonate* + hydric chloride = calcic chloride + *carbonic anhydride* + water:

ammonic chloride + calcic hydrate = calcic chloride + *ammonia* + water.

At 60° C. (140° F.):

potassic carbonate + *ammonic* carbonate = potassic hydric carbonate + *ammonia.*

In hot solutions:

sodic *chloride* + *hydric* sulphate = sodic sulphate + *hydric chloride.*

By ignition:

sodic *sulphate* + *hydric* phosphate = sodic phosphate + *hydric sulphate.*

21. It cannot too soon be understood, concerning changes between substances—acids, bases and salts, in solid, liquid, and gaseous states—strictly chemical in nature and proportions as these changes are, they are not nearly so often determined by the relative degree of chemical power as by co-operating forces—cohesion, adhesion, heat, light, etc.—the circumstances which modify the relative power of affinities.

Furthermore, the student should avoid placing his chief dependence upon generalizations, especially in the early period of his study. Science *rests upon facts.* It is logical to begin at the foundation, and work upwards in the same order in which the investigations of men have established science.

22. While the results of chemical operations are declared to the powers of observation as changes of *masses*, they are represented to the understanding as changes of *molecules*, and as such are expressed in *chemical equations.*

When we observe evidences of a chemical change in any mixture before us, we are assured that some new arrangement of atoms—some alteration of molecules—has occurred. Usually, the evidence shows that certain molecules have broken up, and their atoms have entered into certain new molecules. Now, to state the composition and proportional number of all the molecules which act upon each other, and result in an operation, is to make a chemical equation. The first side of the equation represents the molecules broken up in the operation; the last side, those produced in the operation; each side presenting the same kind and number of atoms, but different molecules. To be prepared to construct the equation, we must know the exact composition—the formulæ—of all the substances brought into the operation, and we must ascertain the composition—the formulæ—of the substances produced in the operation. Having these inviolable data, the formulæ of the molecules, the determination of the *number* of each kind of molecules, necessary "to balance the equation," becomes a simple mathematical calculation. Finally, "the combining number" of each substance in an equation expresses its number of "parts by weight," for large or small quantities, as exemplified in paragraph 24.*

23. In the practice of qualitative analysis, the student necessarily refers to authority for the *composition of precipitates* and other products. For example, when the solution of a carbonate is added to the solution of a calcium salt, a precipitate is obtained; and it has been ascertained by quantitative analysis that this precipitate is normal calcium carbonate, $CaCO_3$, invariably. Were

* Concerning the representation of elements by atoms instead of molecules, in equations, see the footnote under paragraph 18.

The "combining number" of any substance given in an equation is the sum of its molecular or atomic weights as required for the equation. In the first equation in paragraph 18, the combining number of the oxygen is 32. The term "part" should be restricted to the unit of weight, the same for all substances. An atom of hydrogen is one part; an atom of oxygen is equal to sixteen parts.

there no authorized statement of the composition of this precipitate, the student would be unable, without making a quantitative analysis, to declare its formula or to write the equation for its production. When the results of analytical operations are substances of unknown, uncertain, or variable composition, equations cannot be given for them. In much the greater number of cases, but not in all cases, will any acid radical unite with any metal, and, if so, unite as normal salt.

24. By *translating chemical equations into statements of proportional parts by weight*, they are prepared to serve as data for ordinary uses—in operations of manufacture, with large or small quantities, and in quantitative analysis.

For example, in dissolving iron by aid of hydrochloric acid, we have the equation:

$$\underset{55.9}{Fe} + \underset{73.0}{2HCl} = \underset{126.9}{FeCl_2} + 2H$$

Also, in precipitating ferrous chloride by sodium phosphate, we have the equation:

$$FeCl_2 + \underset{142 + 216 = 358.0}{Na_2HPO_4\ [+12H_2O]} = \underset{151.9}{FeHPO_4} + 2NaCl$$

Suppose it is desired to determine from the above:

(1) How much "hydrochloric acid," 32 per cent. HCl, is required to dissolve 100 parts of iron wire?

(2) What quantities of 32 per cent. "hydrochloric acid" and iron wire are necessary to use in preparing 100 parts of absolute ferrous chloride?

(3) What materials, and what quantities of them, may be used in preparing 100 parts of ferrous phosphate?

We write *the combining numbers* of each substance that is to be weighed, under its symbols in the equation. These numbers already express the proportional weights: they may, of course, be changed into other numbers expressing the same proportion to each other. If 56 parts of iron are dissolved by 73 parts of hydrochloric acid, 100 parts of iron require 130 parts of hydrochloric acid. The iron wire is not quite pure iron, but taken as such. The solution of the acid is specified at 32 per cent. The phosphate is weighed in crystals and then dissolved—the water of crystallization being included in the combining number. Then:

1. $\begin{cases} 55.9 : 73.0 :: 100 : x = \text{parts of absolute HCL for 100 parts iron wire.} \\ 32 : 100 :: x : y = \text{parts of 32 p. c. hydrochloric acid for 100 parts of iron.} \end{cases}$

2. $\begin{cases} 126.9 : 73.0 :: 100 : x \\ 32 : 100 :: x : y = \text{parts of 32 p. c. hydrochloric acid for 100 parts of ferrous chloride.} \\ 126.9 : 55.9 :: 100 : x = \text{parts of iron wire for 100 parts of ferrous chloride.} \end{cases}$

3.
$$\begin{cases} 151.9 : 73.0 :: 100 : x \\ 32 : 100 :: x : y = \text{parts of 32 p. c. hydrochloric acid for 100 parts of ferrous phosphate.} \\ 151.9 : 55.9 :: 100 : x = \text{parts of metallic iron for 100 parts of ferrous phosphate.} \\ 151.9 : 358.0 :: 100 : x = \text{parts of cryst. sodium phos. for 100 parts of ferrous phosphate.} \end{cases}$$

Practice in reducing the combining numbers of the terms in an equation to simple parts by weight—grams, grains, ounces, or pounds—is a very instructive exercise, even in the early part of Qualitative Chemistry. It enforces correct and clear ideas of the significance of formulæ and equations, and refers all chemical expressions to the facts of quantitative operations. In pursuing technical chemistry, or advanced chemistry in any direction, this work—in "Chemical Problems" is in constant demand, both as an important means of theoretical study and as a necessary accompaniment of all independent practice.

25. The *chief requirement in qualitative practice* is an experimental acquaintance with the chemical relations of substances, rather than the identification of one after the other by routine methods. The acids and bases, the oxidizing and reducing agents, are all linked together in a network of relations, and the ability to identify one, as it may be presented in any combination or mixture, rests upon acquaintance with the entire fraternity. For example, in the study of an acid, its deportment with all the bases should be learned, all its representative salts should be produced, and the character of these salts should be mentally associated with the respective bases as well as with the acid. The study of sulphuric acid furnishes the best illustration of an important characteristic of lead, calcium, magnesium, and other metals. In any test, the "reagent" should not be held by the student as a mere instrument, but as one of two substances, both of which are under investigation. The earlier the habit of constant generalization is acquired, the sooner will the difficulties of the manipulation clear way. The most direct method of pursuing Analytical Chemistry is *to study chemistry analytically.*

26. It is advisable that *the initiatory qualitative work* be done upon known material—verifying the characteristics of each acid and base, studying the methods of separation, and stating the operations in equations—before attempting actual analysis with unknown material. In this initiatory work, the examination of each acid and each base needs to be so made, or repeated, that the student can obtain, understand, and remember its chemical changes: a mere routine repetition of the simpler analytical tests being worse than waste of time. Reactions having importance in synthesis require as much attention as those important in analysis.

27. The full text of the book, rather than the analytical tables, should be taken as the guide in qualitative operations, especially in those upon known material. The tabular comparisons are commended to attention, especially for review. In the actual analysis, the tables serve mainly as an index to the body of the work. Throughout the practice upon known material, when the

student is engaged upon a base or an acid, and in the study of its reactions, he should refer to a manual of Elementary Chemistry for completion of his acquaintance with the substance in hand. During the analysis of unknown material, the student should constantly consult the more complete works within his reach, such as the dictionaries of Storer, and Watts, and the Hand-book of Gmelin, or the larger manuals of Miller, Schorlemmer, and others. Habits of personal investigation, and of independent search of authorities, when established during qualitative work, form the sure foundation of a good chemical education.

ORDER OF STUDY.

The order of study of qualitative analysis, in the laboratory under the author's charge, varied from year to year, is at this time (1880) about as follows: Preparatory—a drill in "writing salts," to memorize quantivalence and make the notation familiar. Then, FIRST, a study of the solubilities of metallic salts and hydrates, namely: *A*, obtaining all the precipitates by **potassium hydrate** or **sodium hydrate**, with the metals of successive groups, then the same with **ammonium hydrate**, as given in paragraph 33—the student writing equations for all precipitates. *B*, Obtaining the precipitates by potassium **carbonate**, with the successive bases, and formulating the changes (651, 86, 98, 105, etc.) In the same way, the students work out the precipitates with, *C*, the **sulphates** (675, 88, 98, 106, 312); *D*, the **sulphites**; *E*, free **sulphurous acid**; *F*, ammonium **sulphide**; *G*, **hydrosulphuric acid**; *H*, common sodium **phosphate**; *I*, free **phosphoric acid**; *J*, **chlorides**; *K*, **bromides**; *L*, **iodides**; *M*, **iodates**; *N*, potassium **dichromate**; *O*, ammonium **oxalate**. SECOND, a study of the analytical reactions of each base, and then, for the first, practice in the separation of metals from each other, taking them in the order of their groups. THIRD, the analytical reactions of each acid, and then the separations of acids. FOURTH, practice with synthetic operations, devised by the student, for required products, with given materials—equations of all changes being given by the student. Thus, required to make lead sulphide, taking the lead from the metallic state, and the sulphur from calcium sulphate. At this point a full examination is held, and qualification upon all the work passed over is required before going further. FIFTH, the analysis of unknown solid mixtures, each containing from two to seven compounds. The combination of each base, in the greater number, to be determined by the action of solvents upon the mixture. Reports received after analyses of each five, and results of first and second reports preserved. SIXTH, the analysis of mixtures in solution, mostly involving the action of oxidizing and reducing agents. Lastly, a final examination. There is a daily recitation, with the daily laboratory work.

PART I.—THE METALS.

28. Classification of Metals or Bases.—In chemical analysis, the metals are commonly divided into **five groups** according to their deportment, in solution of their salts, with certain general reagents, as follows:

I. Those metals, forming *chlorides insoluble* in water (see 9), are precipitated from the solutions of their salts by the first group reagent, *hydrochloric acid:* **Pb, Ag, Hg_2''.**

II. The metals which in acid solutions form insoluble sulphides, are precipitated from their acidulated solutions by the second group reagent, *hydrosulphuric acid:* **As, Sb, Sn, Pb, Ag, Bi, Cu, Cd, Hg_2'', Hg''.**

III. Those metals which form *sulphides insoluble* in water, but *decomposed by dilute acids*, are precipitated from neutral solutions by the third group reagent, *ammonium sulphide*, which also precipitates two metals in this group as *hydrates:* **Fe, Mn, Co, Ni, Zn, sulphides; Al, Cr, hydrates.**

IV. Of the remaining metals, those having *carbonates insoluble* in water are precipitated from their solutions by the fourth group reagent, ammonium carbonate: **Ba, Sr, Ca, Mg.** If ammonium chloride be present, **Mg** is left for the next group.

V. The metals forming chlorides, sulphides, and carbonates, *soluble in water*, are *not precipitated* by any of the four group reagents, and are left to the fifth group. **K, Na, Li, NH_4.**

29. *Each group reagent will precipitate the metals of preceding groups.* The metals distinguished by being insoluble as chlorides (Group I.), are also insoluble as sulphides (with Groups II. and III.), and as carbonates (with Group IV.) The second group sulphides are precipitated both from acid and from neutral solutions, though the third group sulphides are precipitated from neutral, but not from acid solutions, and second and third group metals form insoluble carbonates, as well as those of Group IV. In the work of analysis, the first group metals may be worked with the second, but thereafter, *the metals found in each group must be completely removed before testing for the next group.* After filtering out a group precipitate, the reagent which produced it should be again carefully applied, with the proper conditions, to the filtrate, before testing it for the next group.

30. Precipitations in the Five Groups of Bases.

Precipitated by	I.	II.	III.	IV.	V.
I. Chlorides.	Pb,† Ag, Hg_2				
II. H_2S in acid sol.	Pb, Ag, Hg	As, Sb, Sn, Bi, Cu, Cd, Hg.			
III. Sulphides.	Pb, Ag, Hg	As,* Sb,* Sn,* Bi, Cu, Cd, Hg.	Zn, Al, Fe, Mn, Cr, Co, Ni.		
IV. Carbonates with NH_4Cl	Pb, Ag, Hg	Sb,* Sn, Bi, Cu, Cd, Hg.	Zn, Al, Fe, Mn, Cr, Co, Ni.	Ba, Sr, Ca.	
Carbonates.	Pb, Ag, Hg	Sb,* Sn, Bi, Cu, Cd, Hg.	Zn, Al, Fe, Mn, Cr, Co, Ni.	Ba, Sr, Ca.	Mg.
Fixed Alkalies.	Pb,* Ag, Hg	Sb,* Sn,* Bi, Cu, Cd, Hg.	Zn,* Al,* Fe, Mn, Cr,* Co, Ni.	Ba,† Sr,† Ca.	Mg.
Ammonia.	Pb, Ag,* Hg	Sb, Sn, Bi, Cu,* Cd,* Hg.	Zn,* Al, Fe, Mn, Cr, Co,* Ni.*		Mg.
Phosphates.	Pb, Ag, Hg	Sb, Sn, Bi, Cu, Cd, Hg.	Zn, Al, Fe, Mn, Cr, Co, Ni.	Ba, Sr, Ca.	Mg, Li.
Oxalates.	Pb, Ag, Hg	Sb, Sn, Bi, Cu, Cd, Hg.	Zn, Al, Fe, Mn, Co, Ni.	Ba,† Sr, Ca.	Mg.†
Sulphates.	Pb			Ba, Sr, Ca.†	
Sulphites.	Pb, Ag, Hg	Sb, Sn, Bi, Cu, Cd, Hg.	Zn, Al, Fe, Mn, Co, Ni.	Ba, Sr, Ca.	Mg.
Bromides.	Pb, Ag, Hg				
Iodides.	Pb,* Ag,* Hg	(Bi) Hg.*			

* Soluble in excess of the reagent. † Not precipitated in dilute solutions.

158677

GROUP V.

The Alkali Metals.

Potassium, . .	**K′ = 39.0**	**Lithium,** . . .	**Li′ = 7.0**
Sodium, . . .	**Na′ = 23.0**	**Rubidium,** . . .	**Rb′ = 85.2**
Ammonium, . .	**$(NH_4)'$=14+4**	**Cæsium,** . . .	**Cs′ = 133.0**

31. The metals of the alkalies are highly combustible, oxidizing quickly in the air, displacing the hydrogen of water * even more rapidly than zinc or iron displaces the hydrogen of acids, and displacing non-alkali metals from their oxides and salts. As elements they are very strong reducing agents, while their compounds are very stable, and not liable to either reduction or oxidation by ordinary means. The five metals, **Cs, Rb, K, Na, Li**, present a gradation of electro-positive or basic power, cæsium being strongest, and the others decreasing in the order of their atomic weights, lithium decomposing water with less violence than the others. Their specific gravities decrease, their fusing points rise, and as carbonates their solubilities lessen, in the same order. In solubility of the phosphate, also, lithium approaches the character of an alkaline earth.

Ammonium is the basic radical of ammonium salts, and as such has the characteristics of an alkali metal. The water solution of the gas ammonia, NH_3 (an anhydride), from analogy is supposed to contain ammonium hydrate, NH_4OH, known as *the volatile alkali.* Potassium and sodium hydrates are *the fixed alkalies* in common use.

32. The alkalies are very **soluble** in water, and *all the important salts of the alkali metals* (including NH_4) *are soluble* in water, not excepting their carbonates, phosphates (except lithium), and silicates; while *all other* metals form hydrates or oxides, either insoluble or sparingly soluble; and carbonates, phosphates, silicates, and certain other salts quite insoluble in water.

Their compounds being nearly all soluble, the alkali metals are *not precipitated* by ordinary reagents, and with few exceptions, their salts do not precipitate each other. **In analysis,** they are mostly separated from other metals by non-precipitation.

33. In accordance with the insolubility in water of the non-alkali hydrates and oxides *the alkali hydrates precipitate all non-alkali metals,* except that ammonium hydrate does not precipitate barium, strontium, and calcium. These precipitates are hydrates, except those of mercury, silver, and antimony.

But certain of the non-alkali hydrates and oxides, though insoluble in water, dissolve in solutions of alkalies; hence, when added in excess, *the alkalies redissolve the precipitates they at first produce with salts of certain metals,* viz.: the hydrates of **Pb, Sn, Sb, Zn, Al,** and **Cr** dissolve in the fixed alkalies;

$$*K + H_2O = KOH + H$$

and oxide of **Ag** and hydrates of **Cu, Zn, Co,** and **Ni** dissolve in the volatile alkali.

Precipitations by Alkali Hydrates (KOH, NaOH, and NH_4OH).

(Note the color of precipitates obtained.)

Barium hydrate, $Ba(OH)_2$, not caused by NH_4OH, sol. in 15 parts water (85).

Strontium " $Sr(OH)_2$, " " " 60 parts water.

Calcium " $Ca(OH)_2$, " " " 700 " (104).

Magnesium " $Mg(OH)_2$, soluble by NH_4Cl, sol. in 6,000 " (114).

Aluminium " $Al_2(OH)_6$, soluble in excess fixed alkali hydrates (145).

Chromium " $Cr_2(OH)_6$, soluble in cold sol. of fixed alkali, precipitated on boiling (154).

Ferrous " $Fe(OH)_2$, slightly soluble by NH_4Cl. Oxidizes in air (174).

Ferric " $Fe_2(OH)_6$ (184).

Manganous " $Mn(OH)_2$, soluble by NH_4Cl. Oxidizes in air (204).

Manganic " $Mn_2(OH)_6$ (214).

Cobalt " $Co(OH)_2$, sol. in excess NH_4OH, and by NH_4Cl (219).

Nickel " $Ni(OH)_2$ " " " " (228).

Zinc " $Zn(OH)_2$, soluble in both fixed and vol. alkalies (235).

Copper " $Cu(OH)_2$, soluble in NH_4OH (with blue color) (273).

Cadmium " $Cd(OH)_2$ " " (colorless) (301).

Bismuth " $Bi(OH)_3$ (289).

Lead " $Pb(OH)_2$, soluble in excess fixed alkalies (309).

Silver oxide, Ag_2O, soluble in excess NH_4OH (330).

Mercurous oxide, Hg_2O (by fixed alkalies) (346).

Mercurous-ammonium chloride, NH_2Hg_2Cl, from Hg_2Cl_2 by NH_4OH (347).

Mercuric oxide, HgO (by fixed alkalies) (356).

Mercur-ammonium chloride, NH_2HgCl, from $HgCl_2$ by NH_4OH (357).

Antimonious oxide, Sb_2O_3, soluble in excess fixed alkalies (403).

Stannous hydrate, $Sn(OH)_2$, " " " (430).

Stannic " $Sn(OH)_4$, " " " (440).

34. Solutions of the alkalies are caustic to the taste and touch, and turn red **litmus** blue; also, the carbonates, acid carbonates, normal phosphates, and

some other salts of the alkali metals, give the "alkaline reaction" with test papers. **Sodium nitroferricyanide**, with hydrogen sulphide, gives a delicate reaction, 668.

35. The hydrates and normal carbonates of the alkali metals are not decomposed by **heat** alone (as are those of other metals), and these metals form the only acid carbonates obtained in the solid state.

36. The fixed alkalies, likewise many of their salts, melt on **platinum foil** in the flame, and slowly vaporize at a bright red heat (distinction from magnesia). All salts of ammonium, by a careful evaporation of their solutions on platinum foil, may be obtained in a solid residue, which rapidly vaporizes, wholly or partly, below a red heat (distinction from fixed alkali metals and magnesium).

37. The hydrates of the fixed alkali metals, and those of their salts most volatile at a red heat, preferably their chlorides, impart strongly characteristic colors to a non-luminous **flame**, and give well-defined **spectra** with the spectroscope.

POTASSIUM.

38. The hydrate, carbonate, dimetallic phosphate, sulphite, nitrite, acetate and normal tartrate are **deliquescent.**

39. None of the potassium salts are quite **insoluble** in water; the *platinic chloride*, *acid tartrate*, silico-fluoride, nitro-phenate, phospho-molybdate, and per-chlorate, being only slightly soluble in water, and quite insoluble in alcohol. The chlorate is but sparingly soluble in cold water, and nearly insoluble in alcohol. Also, the carbonate and sulphate are insoluble in alcohol.

In ordinary qualitative analysis, **potassium compounds are identified** by their flame-color (44), using blue glass to exclude the color of the sodium-flame; also by precipitation of potassium acid tartrate in alcoholic acidified solution (41), or of potassium platinic chloride (40). Both these precipitations are used in quantitative analysis.

40. Platinic Chloride ($PtCl_4$), added to neutral or acid solutions not too dilute, with hydrochloric acid if the compound be not a chloride, **precipitates** *potassium platinic chloride* $(KCl)_2PtCl_4$, crystalline, yellow. Non-alkali bases also precipitate this reagent, and if present must be removed before this test. The precipitate is soluble in 19 parts of boiling water, or 111 parts of water at 10° C. Minute proportions are detected by evaporating the solution with the reagent nearly to dryness, on the water bath, and then dissolving in alcohol; the yellow crystalline precipitate, octahedral, remains undissolved, and may be identified under the microscope.

41. Tartaric acid ($H_2C_4H_4O_6$), or more readily sodium hydrogen tartrate ($NaH\ C_4H_4O_6$), precipitates, from solutions sufficiently concentrated, *potassium hydrogen tartrate*, $KHC_4H_4O_6$, granular-crystalline. If the solution be alkaline, tartaric acid should be added to strong acid reaction. The test must be

made in absence of non-alkaline bases. The precipitate is increased by agitation, and by addition of alcohol. It is dissolved by fifteen parts of boiling water or eighty-nine parts water at 25° C., by mineral acids, by solution of borax, and by alkalies, which form the more soluble normal tartrate, $K_2C_4H_4O_6$, but not by acetic acid, or at all by alcohol of fifty per cent.

42. **Nitrophenic acid,** $HC_6H_2(NO_2)_3O$, picric acid, precipitates, from solutions not very dilute, the yellow, crystalline *potassium nitrophenate,* $KC_6H_2(NO_2)_3O$, insoluble in alcohol, by help of which it is formed in dilute solutions. The dried precipitate detonates strongly when heated.

43. It will be observed that ammonium salts form precipitates with platinic chloride and with tartaric acid, closely resembling those formed with salts of potassium, but the latter is the only fixed alkali which is precipitated by these reagents.

44. Potassium compounds color the **flame** *violet.* A little of the solid substance, or residue by evaporation, moistened with hydrochloric acid, is brought on a platinum wire into a non-luminous flame. The wire should be previously moistened with hydrochloric acid, and held in the flame until it does not color. The presence of very small quantities of *sodium* enables its yellow flame completely to *obscure the violet* of potassium; but owing to the greater volatility of the latter metal, flashes of violet are sometimes seen on the first introduction of the wire, or at the border of the flame, or in its base, even when enough sodium is present to conceal the violet at full heat. Silicates may be fused with pure gypsum, giving vapor of potassium sulphate. The interposition of a **blue glass,** or prism filled with indigo solution, sufficiently thick, entirely cuts off the yellow light of sodium, and enables the potassium flame to be seen. The red rays of the *lithium* flame are also intercepted by the blue glass or indigo prism, a thicker stratum being required than for sodium. If organic substances are present, giving luminosity to the flame, they must be removed by ignition. Certain non-alkali bases interfere with the examination.

45. The volatile potassium compounds, when placed in the flame, give a widely-extended continuous *spectrum,* containing two characteristic lines; one line K α, situated in the outermost red, and a second line, K β, far in the violet rays at the other end of the spectrum.

SODIUM.

46. Of ordinary compounds of sodium, only the hydrate, nitrate, and chlorate are **deliquescent.** The carbonate (10 *aq.*), sulphate (10 *aq.*), sulphite (8 *aq.*), phosphate (12 *aq.*), and acetate (3 *aq.*), are efflorescent.

47. The salts of sodium are freely soluble in water, except the metantimoniate and the silico-fluoride, the latter being sparingly soluble.

Sodium is identified chiefly by its flame-color (50), and by non-precipitation with various reagents. Its soluble salts are weighed in gravimetric operations.

48. Solution of potassium metantimoniate ($KSbO_3$) produces, in neutral or alkaline solutions, a slow-forming, white, crystalline precipitate, $NaSbO_3$, almost insoluble in cold water. The reagent must be carefully prepared and dissolved when required, as it is not permanent in solution. (See under Antimonic Acid, 419.)

49. Sodium platinic chloride, $(NaCl)_2PtCl_4$, crystallizes from its concentrated solutions in red prisms, or prismatic needles (distinction from potassium or ammonium). A drop of the solution to be tested is slightly acidified with hydrochloric acid from the point of a glass rod on a slip of glass, treated with two drops of solution of platinic chloride, left a short time for spontaneous evaporation and crystallization, and observed under the microscope.

50. Sodium compounds color the **flame** intensely *yellow*—the color being scarcely affected by potassium (at full heat), but modified to orange-red by much lithium, and readily intercepted by blue glass. Infusible compounds may be ignited with calcium sulphate. The test is interfered with by some non-alkali bases.

51. The **spectrum** of sodium consists of a single band, Na α, at Fraunhofer's line D, in the yellow of the solar spectrum.

52. The amount of *sodium in the atmosphere*, and in the larger number of substances designed to be "chemically pure," is sufficient to give a distinct but evanescent yellow color to the flame and spectrum.

AMMONIUM.

53. The anhydride, ammonia (NH_3), *gaseous* at common temperatures, dissolves in twice its weight of cold water, forming a volatile solution lighter than water.

54. The "sesquicarbonate" $(NH_4)_4H_2(CO_3)_3$ (1 *aq.*), or tetra-ammonium dihydrogen carbonate, and the phosphate (2 *aq.*), are efflorescent; the nitrate is deliquescent, and the sulphate, slightly deliquescent. The normal carbonate is very instable, and used only in solution.

55. The **solubilities** of the *salts* of ammonium correspond very nearly with those of potassium salts.

Ammonium is found by obtaining the anhydride, ammonia, in vapor (56, 57). Precipitation as mercurammonium iodide (58) is also used. Ammonium platinic chloride is weighed in quantitative work (61). For the nitroferricyanide test, see 668.

56. Ammonia gas (NH_3) escapes from its solutions (having alkaline reaction) at ordinary temperatures, more rapidly when heated; and from its combinations, in any mixture (alkaline, neutral, or acid), by heating with an alkali or alkaline earth (potassium or calcium hydrate).

$$NH_4Cl + KOH = KCl + NH_3 + H_2O$$

57. *Ammonia gas is recognized*, 1st, by its **odor**; 2d, by turning

moistened red **litmus-paper** to blue; 3d, by changing red logwood paper blue; 4th, by rendering paper wet with solution of **cupric sulphate** *blue;* 5th, by *blackening* paper wet with solution of **mercurous nitrate**; 6th, by forming *white fumes* with the **vapors of volatile acids**, vapor of HCl forming solid NH_4Cl; vapor of $HC_2H_3O_2$ forming solid $NH_4\ C_2H_3O_2$, etc.

53. A solution of **potassium mercuric iodide**, $(KI)_2HgI_2$, containing also potassium hydrate—**Nessler's test** *—produces a brown precipitate of nitrogen dimercuric iodide, NHg_2I (dimercur-ammonium iodide, 347, *footnote*), soluble by excess of KI and by HCl; not soluble by KBr (distinction from HgO):

$$NH_3 + 2HgI_2 = NHg_2I + 3HI$$

$$NH_4OH + 2(KI)_2HgI_2 + 3KOH = NHg_2I + 7KI + 4H_2O$$

This very delicate test is applicable to ammonium hydrate or salts; traces forming only a yellow to brown coloration. The potassium mercuric iodide, alone, precipitates the *alkaloids* from *neutral or acid* solutions, but does not precipitate ammonium salts from neutral or acid solutions.

59. Mercuric chloride ($HgCl_2$), forms, in solutions of ammonium hydrate or ammonium carbonate, the "white precipitate" of nitrogen dihydrogen mercuric chloride, NH_2HgCl, or mercur-ammonium chloride. If the ammonium is in a salt, not carbonate, it is changed to the carbonate and precipitated, by addition of mercuric chloride and potassium carbonate previously mixed in solutions (with pure water), so dilute as not to precipitate each other (yellow). This test (Bohlig's) is intensely delicate, revealing the presence of ammonia derived from the air by water and many substances.

60. Add a small quantity of recently precipitated and well-washed **silver chloride**, and, if it does not *dissolve* after agitation, then add a little potassium hydrate solution. The solution of the $AgCl$, *before* the addition of the fixed alkali, indicates free ammonia; *after* the addition of the fixed alkali, ammonium salt. (Applicable in absence of thiosulphates, iodides, bromides, and sulphocyanides.)

61. Platinic chloride, and **tartaric acid**, form precipitates with ammonium, which, in conditions of production, form and color of crystals, and in solubility, *closely resemble the potassium* precipitates with the same reagent. They may be distinguished by the effect of **ignition**, which, in case of ammonium platinic chloride, leaves pure spongy platinum (without KCl), and, in case of ammonium hydrogen tartrate, leaves pure carbon (without K_2CO_3). Also, $NH_4H\ C_4H_4O_6$ is more soluble in water than $KH\ C_4H_4O_6$. *Nitrophenic acid* precipitates ammonium, in solutions not very dilute.

* This reagent may be prepared as follows: To a solution of mercuric chloride add solution of potassic iodide till the precipitate is nearly all redissolved; then add solution of potassium hydrate; leave until the liquid becomes clear, and decant from any remaining sediment.

62. Phosphomolybdate of sodium (494, foot-note) precipitates ammonium from neutral or acid solutions; also precipitates the alkaloids, even from very dilute solutions, and, from concentrated solutions, likewise precipitates **K, Rb,** and **Cs** (all the fixed alkalies, except **Na** and **Li**).

63. Ammonium salts in solution, treated with *chlorine* gas, generate the instable and violently explosive "nitrogen chloride" (NCl_3?) (*a*). The same product is liable to arise from solid ammonium salts treated with chlorine. Gaseous ammonia, and aqueous ammonium hydrate, with chlorine gas, generate free nitrogen (*b*), a little ammonium chlorate being formed if the ammonia is in excess. *Hypochlorites* or *hypobromites* (or chlorine or bromine dissolved in aqueous alkali, so as to leave an alkaline reaction) liberate, from dissolved ammonium salts, all of their nitrogen (as shown in the second equation of *b*); the measure of the nitrogen gas being a means of quantitative estimation of ammonium.—With *iodine*, ammonium iodide and the explosive iodamides (as in equation *c*), are produced; also, in proportion governed by conditions, iodate (*d*), and hypoiodite, may be formed.—Ammonia is liable to atmospheric *oxidation* to ammonium nitrite and nitrate. —*Permanganates* oxidize to nitrate (*e*).—Ammonia is somewhat readily *produced from* nitric acid by strong reducing agents. It is formed with carbonic anhydride, in a water solution of Cyanic acid, and, more slowly, in a water solution of Hydrocyanic acid. It is generated, by fixed alkalies, in boiling solution of Cyanides (*f*); also, in boiling solutions of albuminoids and other nitrogenous organic compounds, this formation being hastened and increased by addition of permanganate (Wanklyn's process). Fusion with fixed alkalies transforms all the nitrogen of organic bodies into ammonia.

a. $NH_4Cl + 6Cl = NCl_3 + 4HCl$

b. $4NH_3 + 3Cl = 3NH_4Cl + N$

$NH_4Cl + 3Cl = 4HCl + N$

c. $2NH_3 + 2I = NH_4I + NH_2I$

d. $6NH_4OH + 6I = 5NH_4I + NH_4IO_3 + 3H_2O$

e. $6NH_4OH + 4H_2Mn_2O_8 = 3NH_4NO_3 + 8MnO(OH)_2 + 5H_2O$

f. $HCN + KOH + H_2O = NH_3 + KCHO_2$ (formate)

64. Heat vaporizes the *carbonate*, and the *haloid* **salts** of ammonium, *undecomposed; decomposes* the *nitrate* with formation of nitrous oxide and water, the *phosphate* and *borate* with evolution of ammonia, and *other salts* with various products.

65. Ammonium compounds impart to the **flame** a faint and evanescent violet color.

LITHIUM.

66. The chloride, chlorate, and many other salts, are very **deliquescent.**

67. The *carbonate*, *phosphate*, and silico-fluoride are only sparingly **soluble** in water; the other salts of lithium are freely soluble in water, and nearly all soluble in alcohol. Lithium is **identified,** chiefly, by spectral analysis and flame-color (70, 71).

68. Sodium phosphate, Na_2HPO_4, precipitates trimetallic *lithium phosphate* Li_3PO_4, soluble in 2,530 parts water; more soluble in solutions of ammonium salts (distinction from magnesium); but much less soluble in strong

solution of ammonia. In dilute solutions, the precipitate forms only after boiling; and addition of sodium hydrate to alkaline reaction, or of ammonia to strong solution, increases the precipitate. Its solution in hydrochloric acid is not at once precipitated by ammonium hydrate in the cold (distinction from alkaline earth metals); and the blow-pipe bead of lithium phosphate, with soda, is transparent (that of alkaline earth metals being opaque).

69. *Nitrophenic acid* forms a yellow precipitate, not easily soluble in water.

70. Compounds of lithium impart to the flame a carmine *red* color, obscured by sodium, but not by small quantities of potassium compounds. Blue glass, just thick enough to cut off the yellow light of sodium, transmits the red light of lithium; but the latter is intercepted by a thicker part of the blue prism, or by several plates of blue glass.

71. The spectrum of lithium consists of a bright red band, Li α, and a faint orange line, Li β. The color tests have an intensity intermediate between those of sodium and potassium.

RUBIDIUM AND CÆSIUM.

72. Of the known elements, these metals possess the extreme of basic power, as appears from the gradation in the properties of the five metals of the alkali group, stated in paragraph 31. Metallic cæsium has not been isolated in mass; rubidium vaporizes more easily than potassium, and decomposes water with more violence. The hydrates of both these metals are very deliquescent, and strongly alkaline. The carbonate of cæsium is soluble in five parts of boiling alcohol—other fixed alkaline carbonates being insoluble in alcohol; but the separation of Cs and Rb carbonates with absolute alcohol is hindered by formation of a double carbonate of both metals, not wholly insoluble in alcohol. The salts of rubidium and cæsium are soluble, except those named in the next paragraph, most nearly coinciding with potassium in precipitation.

73. *Platinic chloride* precipitates, from chlorides or mixtures containing hydrochloric acid, yellow *cæsium platinic* chloride, $(CsCl)_2PtCl_4$, in microscopic octahedral crystals, soluble in 265 parts of boiling water or 2,000 parts of water at 10° C.; also yellow *rubidium platinic chloride*, $(RbCl)_2PtCl_4$, octahedral, soluble in 157 parts boiling water or 649 parts of water at 10° C.—*Tartaric acid*, or sodium hydrogen tartrate, precipitates cæsium hydrogen tartrate only from very concentrated solutions, being dissolved by about 10 parts of water at 25° C. The precipitate of *rubidium hydrogen tartrate*, $RbHC_4H_4O_6$, is much less soluble, requiring 84 parts of water at 25° C. for solution.—*Stannic chloride* precipitates cæsium, from solution with strong hydrochloric acid, as *cæsium stannic chloride*, $(CsCl)_2SnCl_4$, insoluble in strong hydrochloric acid, but soluble in water, and not formed in neutral solution, a distinction and separation from rubidium and all alkaline bases, except ammonium.—*Aluminic sulphate*, or ammonia alum, precipitates, from solutions containing sulphuric acid, *cæsium aluminic sulphate*, $CsAl(SO_4)_2.12H_2O$, soluble in 160 parts of water at 17° C.—*Rubidium aluminic sulphate* is soluble in 44 parts of water at 17° C. The chlorides and other volatile salts of cæsium color the *flame* violet blue; those of rubidium, violet red. Both metals readily give characteristic spectra.

GROUP IV.

74. The Alkaline Earth Metals.

Barium,	**Ba″ = 136.8**
Strontium,	**Sr″ = 87.2**
Calcium,	**Ca″ = 39.9**
Magnesium,	**Mg″ = 23.9**

75. Like the alkali metals (31), **Ba, Sr,** and **Ca oxidize** rapidly in the air at ordinary temperatures—forming alkaline earths—and *decompose water* without the aid of an acid, forming **hydrates**; also these hydrates are formed, with evolution of heat, when the oxides are brought in contact with water. **Mg** oxidizes rapidly in the air when ignited, decomposes water at 100° C., and its oxide—in physical properties unlike the other alkaline earths—slowly unites with water without sensible production of heat. As compounds, these metals are not easily oxidized beyond their quantivalence as dyads, and they require very strong reducing agents to restore them to the elemental state.

76. In *basic power*, **Ba** is the strongest of the four, **Sr** somewhat stronger than **Ca,** and **Mg** much weaker than the other three. It will be observed that the *solubility* of their *hydrates* varies in the *same* decreasing **gradation,** which is also that of their atomic weights; while the solubility of their *sulphates* varies in a *reverse* order, as follows:

77. The *hydrate* of **Ba dissolves** in about 15 parts of water; that of **Sr,** in 60 parts; of **Ca,** in 700 parts; and of **Mg,** in 6,000 parts. The *sulphate* of **Ba** is not appreciably soluble in water; that of **Sr** dissolves in 7,000 parts; of **Ca,** in 400 parts; of **Mg,** in 3 parts. To the extent in which they dissolve in water, alkaline earths render their solutions **caustic** to the taste and touch, and alkaline to **test-papers.**

78. The *carbonates, normal phosphates, silicates,* and some other salts of alkaline earths, are **insoluble** in water (as are those of the bases of the first three groups; see 32). *Magnesium carbonate* is soluble in ammonium salts, whereby its precipitation with the other three is prevented. *Calcium oxalate* and *barium chromate* are insoluble (see table for Group IV., 798); the oxalates of the other alkaline earths and the chromate of strontium are sparingly soluble; chromate of calcium freely soluble.

In qualitative analysis, **the group-separation** of the first three alkaline earth metals is effected, after removal of the first three groups of bases, by precipitation with carbonate in presence of ammonium chloride, after which magnesium is precipitated from the filtrate, as phosphate (28).

79. The **hydrates** of **Ca, Sr,** and **Ba,** in their saturated solutions, necessarily dilute, throw down, from solutions of salts of the metals of the first three groups and of **Mg,** thin precipitates of hydrates of the latter, which precipi-

tates are not soluble in excess of the precipitants (compare 33). In turn, the **fixed alkalies** precipitate, from solutions of **Ba, Sr, Ca,** and **Mg,** so much of the hydrates of these metals as does not dissolve in the water present; but *ammonium hydrate* precipitates only **Mg,** and this but in part, owing to the solubility of $Mg(OH)_2$ in ammonium salts.

80. Solutions containing alkaline earth metals *with phosphoric, oxalic,* boracic, or arsenic acid, necessarily have the acid reaction, as occurs in dissolving phosphates, oxalates, etc., with acids; such solutions are *precipitated by ammonium hydrate* or by any agent which *neutralizes* the solution (19), and, consequently, we have precipitates of this kind in the **third group.**

$$CaCl_2 + H_3PO_4 + 2NH_4OH = CaHPO_4 + 2NH_4Cl + 2H_2O$$
$$CaH_4(PO_4)_2 + 2NH_4OH = CaHPO_4 + (NH_4)_2HPO_4 + 2H_2O$$

81. The *carbonates* of the alkaline earth metals are dissociated by heat, leaving metallic oxides and carbonic anhydride. This occurs with difficulty in the case of **Ba, Sr,** and **Ca;** with readiness in the case of **Mg** (compare 35); hence **ignition** of the carbonates of **Ba, Sr,** and **Ca** causes them to present the alkaline reaction to a slip of moistened litmus-paper.

82. Compounds of **Ba, Sr,** and **Ca** (preferably with **HCl**) impart characteristic colors to the non-luminous **flame,** and readily present well-defined **spectra.**

BARIUM.

83. Most of the soluble salts of barium are **permanent;** the acetate is **efflorescent.**

84. The *chloride,* bromide, iodide, sulphides, ferrocyanides, *nitrate,* chlorate, *acetate,* and *phenylsulphate,* are freely **soluble** in water; the *carbonate, sulphate,* sulphite, *chromate, phosphate,* oxalate, iodate, and silico-fluoride, are **insoluble** in water. The chloride is almost insoluble in strong hydrochloric acid; likewise the nitrate, in strong hydrochloric and nitric acids. The chloride and nitrate are insoluble in alcohol.

Barium may be **separated** from other alkaline earth metals by precipitation as chromate (89), and by its closer precipitation as sulphate (88). The latter precipitation is a sharp distinction from all other metals except lead, strontium, and calcium; and is the operation most used in quantitative analysis of barium, and of sulphates.

85. The **fixed alkali** hydrates precipitate only concentrated solutions of barium salts, as explained by the statement in 77.

86. The **alkali carbonates**—as K_2CO_3 and $(NH_4)_2CO_3$—precipitate, from barium salts in solution, *barium carbonate* ($BaCO_3$) white. (Compare 78 and 19.) The precipitation is promoted by heat, and by ammonium hydrate, but is made slightly incomplete by the presence of ammonium chloride and nitrate.

87. **Barium Carbonate—$BaCO_3$—**is a valuable **reagent** for special purposes, chiefly for separation of third group metals. It is used in the form of the moist precipitate,

which must be thoroughly washed. It is best precipitated from boiling solutions of chloride of barium and carbonate of sodium or ammonium, washed once or twice by decantation, then by filtration, till the washings no longer precipitate solution of nitrate of silver. Mixed with water to consistence of cream, it may be preserved for some time in stoppered bottles, being shaken whenever required for use. When dissolved in hydrochloric acid, and fully precipitated by sulphuric acid, the filtrate must yield no fixed residue.

This reagent removes sulphuric acid (radical) from all sulphates in solution to which it is added (88):

$$Na_2SO_4 + BaCO_3 = BaSO_4 + Na_2CO_3$$

When salts of non-alkali metals are so decomposed, of course, they are left insoluble, as carbonates or hydrates, nothing remaining in solution:

$$FeSO_4 + BaCO_3 = BaSO_4 + FeCO_3$$

$$Fe_2(SO_4)_3 + 3BaCO_3 + 3H_2O = 3BaSO_4 + Fe_2(OH)_6 + 3CO_2$$

The chlorides of the double triads of the third group, namely, *aluminic*, *chromic*, and *ferric* chlorides, are decomposed by barium carbonate; while the other metals of the third group, zinc, manganese, cobalt, nickel, and iron in ferrous combination, are not precipitated from their chlorides by this reagent. But tartaric acid, citric acid, sugar, and other organic substances, prevent the decompositions by carbonate of barium.

88. **Sulphuric acid** (H_2SO_4), and all soluble **sulphates**, precipitate *barium sulphate* ($BaSO_4$) white [77, 19, and 676], slightly soluble in hot concentrated sulphuric acid. *Immediate* precipitation by the (dilute) saturated solution of calcium sulphate distinguishes **Ba** from **Sr** (and of course from **Ca**); but precipitation by the (very dilute) solution of strontium sulphate is a more certain test between **Ba** and **Sr**.

89. **Normal chromates**, as K_2CrO_4, precipitate barium salts (also strontium salts in solutions not very dilute); the yellow precipitate, $BaCrO_4$, being almost insoluble in water, slightly soluble in acetic acid, but soluble in hydrochloric and nitric acids, and moderately soluble in chromic acid.* ($SrCrO_4$, also yellow, is a little more soluble in water than the barium salt.) **Dichromates** (as $K_2Cr_2O_7$) precipitate barium, as normal chromate, *from the acetate*, in solution not dilute (but do not precipitate **strontium**).

90. **Soluble phosphates**, full metallic, or two-thirds metallic, as Na_2HPO_4, precipitate *barium phosphate*, white, consisting of $BaHPO_4$ when the reagent is two-thirds metallic, and $Ba_3(PO_4)_2$ when the reagent is full metallic.

91. **Oxalates**, as $(NH_4)_2C_2O_4$, precipitate barium from solutions not very dilute; as BaC_2O_4, somewhat soluble in oxalic and acetic acids. (Compare 656.)

92. **Hydro-fluosilicic acid**, H_2SiF_6, precipitates white, crystalline $BaSiF_6$, slightly soluble in water, not soluble in alcohol (distinction from **strontium** and **calcium**).

* Soluble in 86,957 parts of water, 3,670 parts of water containing 1 per cent. acetic acid, 2,618 parts of water containing 5 per cent. acetic acid, 2,014 parts of water containing 10 per cent. acetic acid.—Schweitzer: *Contrib. Lab. Univ. Mo.* (1876), p. 30.

93. Solutions of **iodates**, as $NaIO_3$, precipitate, from barium solutions not very dilute, *barium iodate*, $Ba(IO_3)_2$, white, soluble in 600 parts of hot or 1,746 parts of cold water (distinction from the other alkaline earth metals).

94. Barium compounds impart to the **flame** a *yellowish green* color, which appears blue-green when viewed through green glass.

95. The *spectrum* of barium is at once distinguished from all others by the green bands, Ba α, Ba β; a bright band also appears in the yellow and fainter bands in the orange red.

STRONTIUM.

96. The chloride is slightly **deliquescent**; crystals of the nitrate and acetate **effloresce.**

97. In **solubility**, most compounds of strontium closely resemble those of barium (84)—the *hydrate* being a little less soluble, and the *sulphate* and *chromate* more soluble in water than the corresponding barium compounds, and the *silico-fluoride* quite soluble (see 77). The chloride is soluble, the nitrate insoluble in alcohol absolute.

Strontium is **identified,** in the fourth group, after removal of barium, by precipitation with calcium sulphate solution (99); also, quite clearly, by the flame-color and spectrum (100, 101).

98. By its deportment with **carbonates, phosphates,** and **oxalates,** strontium is not to be distinguished from barium; the differing reactions of the two metals with **sulphates, chromates,** and **hydro-fluosilicic acid,** are compared under the head of Barium. Strontium sulphate is soluble in 400 to 500 parts of concentrated nitric or hydrochloric acid.

99. Saturated solution of **calcium sulphate** ($CaSO_4$) slowly produces a faint precipitate of $SrSO_4$, prevented or dissolved by presence of hydrochloric and nitric acids, but insoluble in alcohol. It is almost insoluble in a concentrated solution of ammonium sulphate, which separates it from $CaSO_4$.

100. Strontium compounds color the **flame** *crimson.* In presence of barium the crimson color appears at the moment when the substance, moistened with hydrochloric acid, is first brought into the flame. The paler, yellowish-red flame of calcium is liable to be mistaken for the strontium-flame.

101. The **spectrum** of strontium is characterized by eight bright bands, namely: six red, one orange, and one blue. The orange line, Sr α, at the red end of the spectrum; the two red lines, Sr β and Sr λ, and the blue line, Sr ς, are the most important.

CALCIUM.

102. The *chloride, bromide, iodide, nitrate,* and *chlorate* are **deliquescent;** the acetate is **efflorescent.**

103. The *carbonate, oxalate,* and *phosphate,* are **insoluble** in water; the *hydrate, sulphate, sulphite,* and iodate, are slightly soluble in water (77), but are insoluble in *alcohol.* The chloride, iodide, and nitrate, are soluble in

alcohol. The ferrocyanide is soluble; the potassio-ferrocyanide, insoluble in water.

Calcium is most often **determined** by precipitation as oxalate, after removal of all insoluble sulphates (107).

104. The **fixed alkali hydrates** precipitate *calcium hydrate*, $Ca(OH)_2$, from solutions of calcium salts not very dilute. The precipitate is less soluble in solution of potassium or sodium hydrate, and more soluble in solution of ammonium hydrate than in pure water.

105. In their deportment with soluble **carbonates** (precipitation of $CaCO_3$), and with alkaline **phosphates** (precipitation of $CaHPO_4$ or $Ca_3(PO_4)_2$), solutions of calcium cannot be distinguished from solutions of strontium and barium (86, 90).

106. **Sulphuric acid** and soluble **sulphates** (not calcium sulphate) precipitate $CaSO_4$ from calcium salts, in moderately concentrated solutions, (77 and 19). The precipitate is distinguished from barium and strontium sulphates by dissolving in concentrated solution of *ammonium sulphate.*

107. Alkaline **oxalates,** as $(NH_4)_2C_2O_4$, precipitate *calcium oxalate,* CaC_2O_4, from even dilute solutions of calcium salts. The precipitate is scarcely at all soluble in *acetic* or oxalic acids (separation of oxalic from phosphoric acid), but is soluble in *hydrochloric* and nitric acids. The precipitation is hastened by presence of ammonium hydrate. Formed slowly, from very dilute solutions, the precipitate is crystalline, octahedral. If **Sr** or **Ba** are possibly present in the solution tested, an alkaline *sulphate* must first be added, and *after digesting a few minutes,* if a precipitate appears, $SrSO_4$, $BaSO_4$, or if the solution was concentrated, perhaps $CaSO_4$, it is filtered out, and the oxalate then added to the filtrate (see 798, last column). Observe the precipitate formed by ammonium oxalate in the reagent solution of calcium sulphate. **Ignition** of CaC_2O_4 changes it first to $CaCO_3$, then to CaO, giving alkaline reaction to test-paper.

108. Neutral alkaline **sulphites,** as Na_2SO_3, precipitate $CaSO_3$, nearly insoluble in water, soluble in hydrochloric or nitric acid, and in sulphurous acid. This reaction is common to the alkaline earths.

109. Alkaline **arsenites** precipitate, from neutral calcium solutions, calcium arsenite, $CaHAsO_3$, soluble in acids and in ammonium hydrate. The precipitate forms slowly. Other alkaline earth metals are not precipitated by arsenites, unless in concentrated solutions.

110. Compounds of calcium, preferably the chloride, render the **flame** *yellowish red.* The presence of strontium or barium obscures this reaction, but a mixture containing calcium and barium, moistened with hydrochloric acid, gives the calcium color on its first introduction to the flame.

111. The **spectrum** of calcium is distinguished by the bright green line, Ca β, and the intensely bright orange line, Ca α, near the red end of the spectrum.

MAGNESIUM.

112. The chloride, bromide, iodide, chlorate, nitrate, and acetate (4 *aq.*), are **deliquescent**; the *sulphate* (7 *aq.*), slightly **efflorescent.**

113. The *hydrate, carbonate, phosphate,* and arseniate, are **insoluble** in water; the sulphite, oxalate, and tartrate, sparingly soluble; the chromate, soluble. The hydrate and carbonate are soluble in **ammonium salts**—except ammonium phosphate—(114, *a*).

Magnesium is mostly **determined,** by precipitation as magnesium ammonium phosphate, after removing all carbonates insoluble in ammonium chloride solution (117). For closer exclusion of barium and calcium, see 122.

114. The **fixed alkali hydrates** and the **hydrates** of **barium,** strontium, and **calcium,** precipitate, from magnesium salts in solution, *magnesium hydrate,* $Mg(OH)_2$, nearly insoluble in water, but soluble in ammonium chloride or sulphate (equation *a*).

Ammonium hydrate precipitates half the magnesium as a hydrate, leaving the other half in solution as a double salt of magnesium and ammonium (*b*):

a. $Mg(OH)_2 + 4NH_4Cl = (NH_4Cl)_2MgCl_2 + 2NH_4OH$

b. $2MgSO_4 + 2NH_4OH = Mg(OH)_2 + (NH_4)_2SO_4MgSO_4$

115. Ammonium sulphide forms no precipitate. The normal **carbonates** *of the fixed alkali metals*—as K_2CO_3—precipitate *magnesium basic carbonate* —$Mg_4(CO_3)_3(OH)_2$, variable to $Mg_5(CO_3)_4(OH)_2$. Carbonic acid is liberated in the formation of this basic salt:

$$4MgSO_4 + 4Na_2CO_3 + H_2O = Mg_4(CO_3)_3(OH)_2 + CO_2 + 4Na_2SO_4$$

But in the cold the free CO_2 combines with another portion of $MgCO_3$, to form a soluble supercarbonate:

$$5MgSO_4 + 5Na_2CO_3 + H_2O = Mg_4(CO_3)_3(OH)_2 + MgCO_3.CO_2 + 5Na_2SO_4$$

On boiling, the supercarbonate is precipitated as $MgCO_3$ with escape of CO_2.

116. Ammonium carbonate scarcely precipitates magnesium salts, except in concentrated solutions, owing to the formation of a soluble double carbonate of magnesium and ammonium:

$$MgSO_4 + 2(NH_4)_2CO_3 = MgCO_3(NH_4)_2CO_3 + (NH_4)_2SO_4$$

117. Alkaline **phosphates**—as Na_2HPO_4—precipitate *magnesium phosphate,* $MgHPO_4$, if the solution be not very dilute. But even in very dilute solutions, by the further addition of ammonium hydrate (and NH_4Cl), a crystalline precipitate is slowly formed, *magnesium ammonium phosphate*— $MgNH_4PO_4$. Stirring with a glass rod against the side of the test-tube promotes the precipitation. The addition of ammonium chloride, in this test, prevents formation of any precipitate of magnesium hydrate (114, *b*). The

precipitate dissolves in 15,000 parts pure water, or in 44,000 parts of water containing ammonium hydrate.

118. Alkaline **arseniates**—as Na_2HAsO_4—act with magnesium salts in all respects like the phosphates, giving corresponding precipitates.

119. In the **dry way**, the only characteristic test for magnesium is the *pale rose* color, obtained by igniting, then moistening the compound with solution of **cobalt nitrate**, and again igniting strongly on charcoal. The color is more apparent on cooling, is not intense, and is prevented by presence of many other bases. The spectrum of magnesium, as well as the spectra of most of the metals yet to be described, cannot be obtained by means of the flame, in which their compounds are not volatile. To obtain them, recourse must be had to the electric spark.

120. The Metals of the Alkaline Earths (Ba, Sr, Ca, Mg).

In solution of any salts soluble in water. Most frequently as chlorides, acetates, nitrates (and **Mg**, *also as sulphate).*

Solutions causing Precipitates.	*Results.*			
	Barium.	*Strontium.*	*Calcium.*	*Magnesium.*
Potassium or Sodium Hydrate (79)	Pre. (?) (77)	Pre. (?) (77)	Pre. (77)	Pre. (114)
Ammonium Hydrate	. . . . .	. . . . .	. . . . .	Pre. (114 *b*)
Potassium or Sodium Carbonate (651)	Pre. (86)	Pre.	Pre. (105)	Pre. (115)
Ammonium Carbonate	Pre.	Pre.	Pre.	Partial pre. (116)
Ammonium Carbonate + NH_4Cl (113)	Pre.*	Pre.*	Pre.*	. . . . .
Phosphates, Na_2HPO_4 (709)	Pre.	Pre.	Pre.	Pre. (117)
Sulphates (676) †	Pre. (88)	Pre.	Pre. (106)	. . . . .
Sulphites (687)	Pre.	Pre.	Pre.	Pre.
Oxalates, as $(NH_4)_2C_2O_4$	Pre. (?) (91)	Pre. (?) (98)	CaC_2O_4 ‡	. . . . .
Chromates (164) $K_2Cr_2O_7$	Pre. (yellow)	. . . (89)	. . . . .	. . . . .
Iodates	Pre.	. . . . .	. . . . .	. . . . .

* This precipitate (obtained after removal of Groups I., II., and III.) is a separation from **Mg** and alkali metals. It may be well washed (15), decomposed by hydrochloric or acetic acid (as $CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$), and the resulting solution used for the final tests.

† Saturated solution of calcium sulphate gives a (thin) precipitate, with barium immediately, with strontium not until five, ten, or fifteen minutes have elapsed (99).

‡ Calcium sulphate solution is precipitated by an oxalate : strontium oxalate solution is precipitated by a sulphate such as potassium sulphate or dilute sulphuric acid.

SEPARATION OF THE FOURTH GROUP METALS.

121. Barium, strontium, calcium, and magnesium, may be completely precipitated together, either as *carbonates* or as *phosphates;* but a precipitate of phosphates would be intractable in further operations, owing to the difficulty of removing the non-volatile phosphoric acid. Hence, they are precipitated as carbonates, and this could be done by any alkaline carbonate ; but the necessity for subsequent examination for fixed alkali metals restricts us to ammonium carbonate. Now, this reagent but imperfectly precipitates magnesium (116); and from this difficulty, and also because magnesium is more easily separated from alkali metals than from other alkaline earth metals, the ordinary scheme of separation provides for the precipitation of **Ba, Sr,** and **Ca,** by ammonium carbonate in presence of ammonium chloride, so as to leave **Mg** either with the fifth group, or as a distinct division of the fourth group.

122. The **precipitation of barium, strontium, and calcium,** by ammonium carbonate in the presence of chloride, is not as complete as would be desirable in very delicate analyses. For the carbonates of barium, strontium, and calcium are all slightly soluble in ammonium chloride solution ; and while the prescribed addition of ammonium hydrate, and excess of ammonium carbonate, greatly reduces the solubility of the precipitated carbonates, yet even with these the precipitation is not absolute, though more nearly so with strontium than with barium and calcium. Thus, in quantitative analyses, if barium and calcium are precipitated as carbonates, it must be done in the absence of ammonium chloride or sulphate, and the precipitate washed with water containing ammonium hydrate.

123. But a more accurate precipitation of **barium** is effected by **sulphates,** and of **calcium** by **oxalates,** and these tests may be applied to portions of the filtrate from the precipitation by carbonates, or of the liquid that has given no precipitate by carbonates. Also, the complete removal of barium and calcium is not only a test for traces of these two metals, but it enables us to accept a slight precipitation of phosphate afterwards as conclusive evidence of the presence of magnesium (unless lithium be present). This precautionary work, done after the ordinary work for barium, strontium, and calcium, may be tabulated as follows :

Divide the filtrate from the fourth group into three portions.

Test in I. for **Ba** with a drop of H_2SO_4, leaving some time.	Test in II. for **Ca** with $(NH_4)_2C_2O_4$, leaving some time.

If both **Ba** and **Ca** appear, mix I. and II. ; let the mixture stand ; filter and test the filtrate for **Mg** by Na_2HPO_4 and NH_4OH.

If either **Ba** or **Ca** appears, filter it and test the filtrate for **Mg.**

If neither **Ba** nor **Ca** appears, test portion III. for **Mg.**

124. The solution of **calcium sulphate** can be used to distinguish between barium, strontium, and calcium (88, 99, 106), *provided* that but *one* metal of the group is present, and that the solution be at least moderately *concentrated,* and *not* notably *acid.*

125. The unlike solubilities in **alcohol,** of the **chlorides** and **nitrates** of barium, strontium, and calcium (84, 97, 103) enable us to separate them quite closely by absolute alcohol, and approximately by "strong alcohol," as follows :

Dissolve the carbonate precipitate in **HCl,** evaporate to dryness on the water-bath, rub the residue to a fine powder in the evaporating dish, and digest it with alcohol. Filter through a small filter, and wash with alcohol.

Residue, $BaCl_2$.	*Filtrate* $SrCl_2$ and $CaCl_2$.
Dissolve in water, test with $CaSO_4$, etc.	Evaporate to dryness, dissolve in water, change to nitrates by precipitating with $(NH_4)_2CO_3$, washing, and dissolving in HNO_3. Evaporate the nitrates to dryness, powder, digest with alcohol, filter and wash with alcohol.

Residue, $Sr(NO_3)_2$.	*Filtrate,* $Ca(NO_3)_2$.
Precipitation by $CaSO_4$ in water solution; flame test, etc.	Precipitation by H_2SO_4 in alcohol solution; by $(NH_4)_2C_2O_4$, etc.

126. Or, the alcoholic filtrate of $SrCl_2$ and $CaCl_2$ may be precipitated with (a drop of) sulphuric acid, the precipitate filtered out and digested with solution of $(NH_4)_2SO_4$ and a little NH_4OH (106). *Residue,* $SrSO_4$. *Solution* contains $CaSO_4$, precipitable by oxalates.

127. Approximate separation of barium and strontium from calcium may be effected by **ignition** of their *carbonates* at a white heat for a few minutes, on platinum foil. Barium and strontium become caustic sooner than calcium (81), and hence dissolve when the mass is treated with water. This operation is sometimes resorted to in obtaining **spectra** of barium and strontium, which are obscured by much calcium.

SEPARATION OF MAGNESIUM FROM THE ALKALI METALS.

128. By **ignition** on platinum foil, magnesium compounds do *not vaporize,* as do those of ammonium, *nor melt,* as do many compounds of fixed alkalies (36). Magnesium is the only one of these metals **precipitated** by ordinary salts—viz., by *phosphates,* carbonates and hydrates.

129. The presence of magnesium slightly impairs the delicacy of the *flame-test* for the fixed alkali metals, and entirely prevents their recognition or separation by precipitations. *Phosphate of ammonium* will **remove magnesium** from solution; but, after evaporating the filtrate and igniting its residue, the phosphoric acid remains—combined with the fixed alkali metals, if they are present. Thus:

$(NH_4)_2HPO_4$ (excess of reagent), ignited $= HPO_3 + 2NH_3 + H_2O$, and

$2(NH_4)_2HPO_4 + 4KCl$, on ignition $= K_4P_2O_7 + 4NH_4Cl + H_2O$

The residual phosphates of the alkali metals, when moistened with hydrochloric acid, give the flame-tests, but the residue of phosphoric acid obstructs the analysis. The phosphoric acid may be removed by acetate of lead, and the excess of lead by hydrosulphuric acid.

130. A more convenient method of removing magnesium is to precipitate it with **solution of barium hydrate,** and filter, and remove the excess of barium hydrate from the filtrate by addition of sulphuric acid, filtering again.

GROUP III.

131. The Metals of the Earths, and the more Electro-Positive of the Heavy Metals.

Aluminium . . . . $Al = 27.3$ Al_2^{VI}

Chromium . . . . $Cr = 52.4$ { Cr_2^{VI} ; Chromic acid, $H_2Cr^{VI}O_4$

Iron	Fe = 55.9	Fe''	In ferrous compounds.
		Fe_2^{VI}	" ferric "
Manganese . .	Mn = 54.8	Mn''	" manganous "
		Mn_2^{VI}	" manganic "
		Mn^{IV}	" pyrolusites.
		$H_2Mn^{VI}O_4$	Manganic acid,
		$H_2Mn_2O_8$ or $HMnO_4$	Permanganic acid,
Cobalt . . .	Co = 58.6	Co''	In cobaltous compounds.
		Co_2^{VI}	" cobaltic "
Nickel . . .	Ni = 58.6	Ni''	
Zinc . . .	Zn = 64.9	Zn''	

Uranium	Ur = 240.0	Ur'''' and Ur^{VI}
Indium	In = 113.4	In_2^{VI} and In''''
Beryllium	Be = 9.0	Be''
Thorium	Th = 231.5	Th''''
Zirconium	Zr = 90.0	Zr''''
Cerium	Ce = 141.3	Ce''' and Ce''''
Lanthanum	La = 139.0	La'''
Didymium	D = 145.0	D'''
Titanium	Ti = 48.0	Ti'', Ti_2^{VI}, and Ti''''
Tantalum	Ta = 182.0	Ta^{V}
Niobium	Nb = 94.0	Nb^{V}
Yttrium	Y = 93.0	Y'''
Erbium	E = 169.0	E'''
Vanadium	V = 51.2	V''' and V^{V}

132. The metals above named gradually oxidize at their surfaces in the air, and their oxides are not decomposed by heat alone. Zinc, iron, cobalt, nickel, and, with more difficulty, manganese, chromium, and most of the other metals of the group, are reduced from their oxides by ignition at white heat with charcoal. They are all reduced from oxides by the metals of the alkalies. Iron is gradually changed from ferrous to ferric combinations by contact with the air. Chromium and manganese are oxidized from bases to acid radicals by ignition with an active supply of oxygen in presence of alkalies; these acid radicals acting as pretty strong oxidizing agents.

133. The *oxides* and *hydrates* of third group metals are **insoluble** in water, hence they are precipitated from all their salts by **alkalies.** In the case of *zinc*, the precipitate redissolves in all the alkalies; the *aluminium* hydrate redissolves in the fixed alkalies, but very slightly in ammonium hydrate; the precipitate of *chromium* redissolves in cold solution of fixed alkalies, precipitating again on boiling; the hydrates of *cobalt* and *nickel* dissolve in ammonium hydrate. The oxides of **Al, Cr,** and **Fe,** after ignition, are difficultly soluble by acids.

The presence of tartaric acid, citric acid, sugar, and some other **organic substances,** *prevents the precipitation of bases of this group by alkalies.*

134. Salts of ammonium (as NH_4Cl) dissolve moderate quantities of the hydrates of manganese, zinc, cobalt, nickel, and ferrous hydrate; but, so far from dissolving the hydrate of aluminium, they lessen its slight solubility in ammonium hydrate.

135. It thus appears that **ammonium hydrate,** with **ammonium chloride,** the latter necessary on account of magnesium, manganese, aluminium, will fully precipitate only **aluminium, chromium,** and **ferricum** of the important metals named in third group. In many plans of separation these three metals constitute a separate group, and we shall refer to them as Division First of the group.

136. Ammonium sulphide precipitates *all* the metals of the third group from neutral or ammoniacal solutions, as follows: The *sulphides* of the group —those of **Fe, Mn, Co, Ni,** and **Zn**—are *soluble in dilute acids,* which acids keep them in solution during the second group precipitation; but are *insoluble in water,* which enables them to be precipitated by alkaline sulphides, and separated from the fourth and fifth groups. The other two metals, **Al** and **Cr,** do not form sulphides, in the wet way, but are precipitated as *hydrates* by alkaline sulphides.

137. Hydrosulphuric acid scarcely precipitates the metals of this group, unless it be from some of their acetates—owing to the solubility of the sulphides in the acids, which would be set free in their formation. Thus, this change cannot occur—

$$FeCl_2 + H_2S = FeS + 2HCl$$

—because the two products would decompose each other (19). Therefore, neutralized hydrosulphuric acid—a soluble sulphide—is employed for this group, and in a neutral or ammoniacal solution. As most of the *chemically normal* salts of heavy metals have an acid reaction to test-paper, we can only assure ourselves of the requisite neutrality by adding sufficient ammonium hydrate, which itself precipitates the larger number of the bases, as we have just seen (133). But the resulting precipitate of hydrate, as $Fe(OH)_2$, is immediately changed to sulphide, **FeS,** by subsequent addition of ammonium sulphide; as the student may observe, by the alteration in the color of the precipitate.

Ferric and manganic salts are **reduced** to ferrous and manganous salts, by hydrosulphuric acid, in solution, with a *precipitation of sulphur,* and the corresponding reaction occurs with chromates (171 *a,* 214, 166 *a*).

138. Soluble **carbonates** precipitate all the metals of this group, in accordance with the general statement for bases not alkali. With aluminium and chromium, the precipitates dissolve sparingly in excess of potassium or sodium carbonate; with zinc, the precipitate dissolves in excess of ammonium carbonate. In the case of ferrous and manganous salts, the precipitates are

normal carbonates; with zinc, cobalt, and nickel salts, they are basic carbonates; while, with ferric, aluminic, and chromic salts, the precipitates are almost or quite wholly hydrates. Barium carbonate precipitates the pseudo-triads, which, in the cold and from salts not sulphates, is a separation from the other bases of this group.

139. Soluble **phosphates** precipitate these as they do other non-alkali bases. The acid solutions of phosphates of the metals of the third group are precipitated by neutralization. The recently precipitated phosphates, of all the metals of this group which form sulphides, are transformed to sulphides by ammonium sulphide:

$$FeHPO_4 + (NH_4)_2S = FeS + (NH_4)_2HPO_4.$$

Hence, the only phosphates which may occur in a sulphide precipitate are those of **Al, Cr, Ba, Sr, Ca,** and **Mg.**

140. The metals of the third group are not easily reduced from their compounds to the metallic state by **ignition** before the blow-pipe, even *on charcoal*, except zinc, which then vaporizes. Three of them, however—iron, cobalt, and nickel—are reducible to magnetic oxides. The larger number of them give characteristic colors to **beads** of borax and of microcosmic salt, fused on a loop of platinum wire before the blow-pipe. None of them color the **flame** or give **spectra,** unless vaporized by a higher temperature than that of Bunsen's burner.

ALUMINIUM.

141. A silver-white metal, somewhat harder than zinc, fusible at 700° C. (1292° F.), non-volatile, and suffering only superficial oxidation by ignition in the air.

142. The metal is readily **soluble** in hydrochloric acid and in aqueous fixed alkalies, with evolution of hydrogen (compare 233 *b*), but it is not readily dissolved by nitric acid, or dissolved by sulphuric acid, or by ammonium hydrate. The anhydrous aluminium oxide dissolves with difficulty in acids, unless previously fused with alkalies or alkaline carbonates. Sulphuric acid dissolves aluminium from some native compounds.

143. The *chloride* and *bromide* are **deliquescent** and instable. The iodide is known only in solution, the cyanide is not known, the acetate is deliquescent. Aluminium is the most representative constituent of that large class of isomorphous double salts, called **alums,** permanent or slightly efflorescent, as $KAl(SO_4)_2.12\,aq.$, or $K_2Al_2(SO_4)_4.24\,aq.$

144. The *oxide*, *hydrate*, and *phosphate*, are the principal **insoluble** combinations. The carbonate and sulphide are instable, and are not formed by ordinary operations. Most insoluble salts of aluminium are changed to soluble compounds by action of fixed alkali hydrates. In **analysis,** aluminium is obtained in the First Division of Group III, by precipitation, by excess of ammo-

nium hydrate, with ammonium chloride (135); then separated from the other members of the First Division by solution with excess of potassium or sodium hydrate (145). Excess of fixed alkali hydrate in boiling solution leaves only aluminium and zinc, of the third group metals, dissolved, and it is separated from zinc, by non-precipitation with sulphides, and by precipitation with excess of ammonium hydrate.

145. The **alkali hydrates** precipitate *aluminium hydrate*, grayish-white, gelatinous, $Al_2(OH)_6$, *soluble in fixed alkali hydrates*, slightly soluble in ammonium hydrate, though not so if ammonium chloride be present (134):

$$Al_2Cl_6 + 6KOH = Al_2(OH)_6 + 6KCl$$
$$Al_2(OH)_6 + 2KOH = K_2Al_2O_4* + 4H_2O$$

This alkaline solution of aluminium differs from that of zinc, both in not being at all precipitated by boiling, and in being precipitated by excess of ammonium chloride, more readily when heated:

$$K_2Al_2O_4 + 2NH_4Cl + 4H_2O = Al_2(OH)_6 + 2KCl + 2NH_4OH$$

Sufficient ammonium chloride must be added, first to salify the **free** potassium or sodium hydrate.

146. **Hydrosulphuric acid** does not precipitate aluminium from any combination; but **ammonium sulphide** precipitates the *aluminium hydrate*, $Al_2(OH)_6$, with evolution of hydrosulphuric acid (136):

$$Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = Al_2(OH)_6 + 3(NH_4)_2SO_4 + 3H_2S$$

147. Alkali **carbonates** also precipitate the *hydrate*, with evolution of carbonic anhydride—the precipitate being sparingly soluble in excess of sodium or potassium carbonate, scarcely at all soluble in excess of ammonium carbonate:

$$Al_2(SO_4)_3 + 3K_2CO_3 + 3H_2O = Al_2(OH)_6 + 3K_2SO_4 + 3CO_2$$

Barium carbonate, on digestion in the cold, precipitates the whole of aluminium from its chloride, as hydrate mixed with a little basic salt (compare 191).

Basic acetate of aluminium is precipitated as follows: To the solution of aluminium salt add a little sodium or ammonium **carbonate**, as much as can be added without leaving a precipitate on stirring, then add excess of **sodium or ammonium acetate**, and boil for some time, when the precipitation at length becomes very nearly complete.

148. Alkali **phosphates** precipitate *aluminium phosphate*, white, $Al_2(PO_4)_2$, soluble in the fixed alkali hydrates, not in acetic acid.

* Or $Al_2O_3(OK)_2$. A series of volumetric determinations, made by Mr. J. N. Ayres and the author (*Jour. Am. Chem. Soc.*, Feb., 1880), give results according closely with this formula for potassium aluminate, and $Na_2Al_2O_4$ for sodium aluminate—as fixed by the constituents of the solutions when the precipitates are held dissolved by least excess of alkali.

To separate **Al** *from* PO_4, fuse the precipitate or powdered substance with 1½ parts finely divided **silica** and 6 parts dried **sodium carbonate** in a platinum crucible, for half an hour. Digest the mass for some time in water ; add **ammonium carbonate** in excess, filter and wash. The residue consists of aluminium sodium silicate ; the solution contains the PO_4, as sodium phosphate. The **Al** can be obtained from the residue by dissolving it in **hydrochloric acid,** evaporating to dryness to render the silica insoluble. Treat with hydrochloric acid, and filter : the filtrate containing aluminium chloride.

Also, **Al** (and ferricum) may be separated from PO_4 by dissolving in **hydrochloric acid,** adding **tartaric acid** and then **ammonia,** and digesting some time with the mixture of **magnesium sulphate, ammonium chloride,** and **ammonium hydrate.** The filtrate contains most of the aluminium.

149. Sodium thiosulphate precipitates, from aluminium salts, in neutral solutions, *aluminium hydrate,* with free sulphur, and liberation of sulphurous anhydride (*a*). The liquid should be dilute, and boiled till it no longer gives the odor of sulphur dioxide, This precipitation (Chancel's) is a separation from iron. See Table at 242½. If phosphates are present, and sodium acetate with acetic acid to acidify slightly, the aluminium is precipitated as *phosphate.*

a. $Al_2(SO_4)_3 + 3Na_2S_2O_3 + 3H_2O = Al_2(OH)_6 + 3S + 3SO_2 + 3Na_2SO_4$

Potassium ferrocyanide very slowly precipitates a white mixture of *aluminium hydrate and ferrous cyanide* with formation of hydrocyanic acid. Ferricyanides do not precipitate aluminium ; neither do oxalates. Solution of **borax** precipitates an acid aluminium borate, quickly changed to *aluminium hydrate.* In very concentrated solutions, addition of **potassium sulphate** causes the crystallization of alum, *potassium aluminium sulphate,* in regular octahedrons or cubes.

150. Compounds of aluminium are not reduced to the metal, but most of them are reduced to the oxide, by **ignition** on charcoal. If now this residue is moistened with solution of **cobaltous nitrate,** and again strongly ignited, it assumes a *blue* color. This test is conclusive only with infusible compounds, and applicable only in absence of colored oxides.

CHROMIUM, AS A BASE.

151. Chromium, in the metallic state, is steel-gray, crystallizable, permanent in the air, and is very rare. **Chromic oxide,** Cr_2O_3, is a bright green powder, constituting a rare variety of "chrome green," the more common sorts being mixtures of chromate of lead (chrome yellow) and ferrocyanide of iron (prussian blue). It is with difficulty **dissolved** by hydrochloric and sulphuric acids. **Chromic hydrate** is easily dissolved by acids. In several respects the combinations of chromium are analogous to those of aluminium.

152. There are two modifications of chromic salts, one having a green **color** and the other violet to red. There are many double salts. The chloride is **deliquescent.**

153. *Chromic oxide, hydrate,* and *phosphate,* are **insoluble** in water. The carbonate and sulphide are not formed in the wet way. There are modifications of the chloride and sulphate insoluble in water. In **analysis,** chromium

is precipitated in the third group as a hydrate, and identified by the oxidation of this hydrate to a salt of chromic acid, known by its colored precipitates with lead and barium salts (159 *d*). It is separated in the First Division of the group (135 and 154).

154. The fixed alkali hydrates, as **KOH**, precipitate the bluish-green *chromic hydrate*, $Cr_2(OH)_6$. Other hydrates are formed in certain conditions. The precipitate redissolves readily in excess of the alkalies while cold, the solution being green.

Long boiling reprecipitates the whole of the chromium, as hydrate; the same result is effected on heating by addition of ammonium chloride (compare 145, last equation).

Ammonium hydrate precipitates *chromic hydrate*, which but slightly redissolves with excess of the alkali in the cold and all reprecipitates readily on heating. The precipitate from solutions of green chromic salts is grayish green, dissolving with acids to form a green solution again; from solutions of violet chromic salts, the precipitate is grayish-blue, dissolving with acids to reproduce the violet solution. The tints are, however, modified by the degree of concentration of solution, and by other conditions.

155. Hydrosulphuric acid does not affect solutions of chromic salts, whether acid, neutral, or alkaline; and **ammonium sulphide** precipitates *the hydrate*, with evolution of hydrosulphuric acid. The equation corresponds to that for aluminium (146).

Both hydrosulphuric acid and ammonium sulphide, acting on **Chromic Acid** or chromates, abstract oxygen, and form the chromic base. In the neutral solution for the third-group precipitation, this deoxidation leaves the chromium in the precipitate as a hydrate; whence it is that the occurrence of chromium in the third group of bases, as frequently as otherwise, must be referred to the existence of combinations of chromic acid, in the material examined. (See 166 *a*.)

156. Alkali **carbonates** precipitate chromium *hydrate*, nearly free from carbonate (138), somewhat soluble in excess of potassium or sodium carbonate:

$$Cr_2(SO_4)_3 + 3K_2CO_3 + 3H_2O = Cr_2(OH)_6 + 3K_2SO_4 + 3CO_2$$

Barium carbonate precipitates chromium from its solutions (better from the chloride), as a hydrate with some basic salt, the precipitate being complete after long digestion in the cold. For removal of excess of reagent, consult 191.

157. Soluble **phosphates**—as Na_2HPO_4—precipitate *chromic phosphate*, $Cr_2(PO_4)_2$, insoluble in acetic acid. **Cyanide of potassium** precipitates the hydrate. **Ferrocyanides**, and **oxalates**, cause no precipitates. **Potassium chromate** colors an acid solution of chromic salt brown-yellow; on addition of ammonium hydrate, a precipitate of the same color is obtained, chromic chromate.

158. Chromic oxide and chromic salts dissolve in **beads of microcosmic salt**, and of borax, before the blow-pipe, in both reducing and oxidizing flames, with a yellowish-green tint while hot, becoming emerald green when cold.

159. Chromic oxide and chromic salts are OXIDIZED TO CHROMIC ACID and chromates by various **strong oxidizing agents** : By treating with **bromine**, in alkaline solution, (*a*) ; by boiling with **hypochlorites** in alkaline solution, (*b*) ; by boiling with **lead dioxide**, (*c*) ; by fusing with alkaline **nitrate** and carbonate (*d*). Further, see 856.

a. $Cr_2(OH)_6 + 6Br + 10NaOH = 2Na_2CrO_4 + 6NaBr + 8H_2O$

b. $Cr_2(OH)_6 + 4NaOH + 3NaClO = 2Na_2CrO_4 + 3NaCl + 5H_2O$

c. $Cr_2(OH)_6 + 2KOH + 3PbO_2 = 2PbCrO_4 + K_2PbO_2 + 4H_2O$

The yellow lead chromate is separated after neutralizing with acetic acid.

d. $Cr_2O_3 + 2NaNO_3 + Na_2CO_3 = 2Na_2CrO_4 + 2NO + CO_2$

The fused mass, dissolved in water, filtered and neutralized with acetic acid, gives the evidences of chromates, as stated in 163, 164.

CHROMIC ACID.

160. Chromic anhydride, CrO_3, commonly called "chromic acid," is a scarlet-red solid, usually in acicular crystals, very deliquescent in the air, and soluble in a small proportion of water. It is a very powerful oxidizing agent, acting explosively with combustible substances, and as a caustic to living tissues. Its soluble salts are poisonous, and have a bitter metallic taste.

161. The alkali metals form yellow **normal chromates** and reddish **dichromates** ; most other metals form normal chromates, yellow or red ; a few form only basic or instable chromates. Most soluble salts of chromic acid crystallize in **permanent** forms ; sodic normal chromate is efflorescent.

162. All the chromates of the alkali metals, and those of magnesium, calcium, zinc, and copper, are **soluble** in water ; strontium and mercuric chromates, sparingly soluble ; barium, manganous, bismuth, mercurous, silver, and lead, chromates **insoluble** in water. Nitric acid transposes chromates.

163. Lead salts precipitate, from normal and from superchromates, the yellow, *lead chromate*, $PbCrO_4$, slowly soluble in nitric acid, not soluble in acetic acid, difficultly soluble in potassium hydrate.

164. Barium salts precipitate from solutions of normal chromates, also from concentrated solutions of superchromates, the normal *barium chromate*, yellow, soluble in hydrochloric and nitric acids, slightly soluble in chromic acid (89).

165. Silver salts precipitate *silver chromate*, Ag_2CrO_4, dark red, soluble in nitric acid and in ammonia. **Mercurous nitrate** precipitates *mercurous chromate*, Hg_2CrO_4, dark red, decomposed by ignition into chromic oxide, oxygen, and vapor of mercury.

166. Chromic anhydride and chromates are DEOXIDIZED TO CHROMIC compounds by various **reducing agents**. The following instances occur frequently in qualitative analysis : other examples are given, in the study of Chromate reductions, 857.

Hydrosulphuric acid, in acid solutions, quickly causes reduction to a green chromic salt solution (*a*). At first the sulphur is all precipitated, white in the green liquid ; but on

warming, it slowly dissolves by oxidation to sulphurous acid, with precipitation of brown basic chromic chromate (*b*), the action being continued, with slow oxidation of the sulphurous acid (*c*) [H. B. Parsons]. **Ammonium sulphide,** in solutions neutral or alkaline, precipitates *chromic hydrate,* green, with oxidation of the sulphide. The precipitate is liable to contain sulphur. In case of yellow or supersulphide of ammonium, it is stated that thiosulphate is obtained in the solution (*d*).

a. $2H_2CrO_4 + 6HCl + 3H_2S = Cr_2Cl_6 + 3S + 8H_2O$
b. $6H_2CrO_4 + 3S = 2Cr_2O_2CrO_4 + 3H_2SO_3 + 3H_2O$
c. $2H_2CrO_4 + 3H_2SO_3 = Cr_2(SO_4)_3 + 5H_2O$
d. $K_2Cr_2O_7 + (NH_4)_2S_2 + 4H_2O = Cr_2(OH)_6 + K_2S_2O_3 + 2NH_4OH$

167. By **ignition** on charcoal, the carbon deoxidizes chromic anhydride, free or combined, and a *green mass,* Cr_2O_3, is left. Chromates give, in the **beads,** the results described for chromic base, in 158.

IRON.

168. Iron **dissolves,** in hydrochloric acid, and in dilute sulphuric acid, to ferrous salts, with liberation of hydrogen (*a*); in moderately dilute nitric acid, with heat, to ferric nitrate, liberating chiefly nitric oxide (*b*); in cold dilute nitric acid, forming ferrous nitrate with production of ammonium nitrate (*c*), of nitrous oxide (*d*), or of hydrogen (*e*):

a. $Fe + H_2SO_4 = FeSO_4 + 2H$
b. $2Fe + 8HNO_3 = Fe_2(NO_3)_6 + 2NO + 4H_2O$
c. $4Fe + 10HNO_3 = 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$
d. $4Fe + 10HNO_3 = 4Fe(NO_3)_2 + N_2O + 5H_2O$
e. $Fe + 2HNO_3 = Fe(NO_3)_2 + 2H$

In dissolving the iron of commerce in hydrochloric acid, the **carbon** which it always contains, so far as combined in the carbide of iron, will pass off in gaseous hydrocarbons, and so far as uncombined will remain undissolved, as graphitoid carbon.

169. Iron acts as a base in **two kinds of salts:** the ferrous and the ferric; both are stable, in considerable variations of temperature, when undisturbed by other substances; but the ferrous compounds are changed to ferric by contact with the air, and by oxidizing agents generally; while the ferric compounds are permanent in the air, but are changed to ferrous combinations by reducing agents. In the systematic course of analysis, by the treatment necessary in separation from other metals, the ferric compounds are reduced to ferrous compounds, and then, by air and by reagents, partially or wholly changed to ferric compounds again, and the original substance must always be tested for determination whether ferrous or ferric. The metal oxidizes in moist air to ferric oxyhydrate, $Fe_4O_3(OH)_6$. By ignition in the air, chiefly ferrous oxide is formed. Scale oxide is $(FeO)_6Fe_2O_3$. By fusing ferric oxide with

potassium nitrate, there is formed potassium ferrate, $K_2Fe^{VI}O_4$, soluble in water, instable, but capable of precipitating a permanent barium ferrate.

170. FERROUS COMPOUNDS ARE OXIDIZED to ferric compounds by nearly all **oxidizing agents**, such as chlorine, calcium hypochlorite, potassium chlorate with hydrochloric acid (*a*); bromine (*b*); nitric acid (814); silver nitrate (836); chromates (857); permanganates (199 *b*); auric chloride (475). Further, see 854.

a. $2FeCl_2 + 2Cl = Fe_2Cl_6$

$6FeSO_4 + 6Cl = 2Fe_2(SO_4)_3 + Fe_2Cl_6$

$2FeSO_4 + 2Cl + H_2SO_4 = Fe_2(SO_4)_3 + 2HCl$

b. $2FeCl_2 + 2Br + 2HCl = Fe_2Cl_6 + 2HBr$

Ferrous salts, therefore, are *reducing agents* of considerable power.

171. FERRIC COMPOUNDS ARE DEOXIDIZED by many **reducing agents**—as hydrosulphuric acid (*a*); sulphurous acid (*b*); thiosulphates (*c*); stannous chloride (*d*); metallic zinc (*e*). The same occurs in precipitation by ammonium sulphide (187). Grape sugar effects the reduction on boiling for some minutes. For a study of the reduction of ferric compounds, see 855.

a. $Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S$

b. $Fe_2Cl_6 + H_2SO_3 + H_2O = FeSO_4 + FeCl_2 + 4HCl$

c. $Fe_2Cl_6 + 2Na_2S_2O_3 = 2FeCl_2 + 2NaCl + Na_2S_4O_6$

d. $Fe_2Cl_6 + SnCl_2 = 2FeCl_2 + SnCl_4$

e. $Fe_2(SO_4)_3 + Zn = 2FeSO_4 + ZnSO_4$

Ferric salts, then, act as *oxidizing agents* of moderate power.

172. **FERROUS** salts, in crystals and in solution, have a light green **color.** The oxide is black; the salts slightly redden **litmus.** The sulphate (7 *aq.*) is **efflorescent**; the chloride, bromide, iodide, and citrate, are **deliquescent**; the hydrate, chlorate, and sulphite, are especially instable.

173. The *hydrate*, oxide, *carbonate*, *sulphite*, *phosphate*, borate, oxalate, cyanide, ferrocyanide, *ferricyanide*, tartrate, and tannate, are **insoluble** in water. In **analysis**, ferrous compounds are identified as ferrous, by their blue precipitate with ferricyanide (178); and, as iron, by the red solution which, after oxidation, they form with sulphocyanate.

174. The **alkali hydrates** precipitate *ferrous hydrate*, $Fe(OH)_2$, white if pure, but seldom obtained sufficiently free from ferric hydrate to be clear white, and quickly changing, in the air, to ferroso-ferric hydrate, of a dirty-green to black color, then to ferric hydrate (184), of a reddish-brown color. The fixed alkalies adhere to this precipitate. **Ammonium chloride** or sulphate, to a slight extent, dissolves the ferrous hydrate or prevents its formation (compare 134).

175. The soluble **carbonates** precipitate, from purely ferrous solutions, *ferrous carbonate*, $FeCO_3$, white if pure, but soon changing, in the air, to the reddish-brown ferric hydrate (184).

176. Hydrosulphuric acid does not disturb ferrous salts—the acetate being only slightly precipitated, as explained in 137. **Ammonium sulphide** precipitates *ferrous sulphide*, **FeS**, black. The moist precipitate is slowly converted, in the air, to ferrous sulphate; and afterward, to basic ferric sulphate, $Fe_2O(SO_4)_2$.

177. Alkali **phosphates**—as Na_2HPO_4—precipitate two-thirds metallic *ferrous phosphate*, $FeHPO_4$, mixed with the full-metallic salt, $Fe_3(PO_4)_2$, white to bluish-white. By the addition of an alkali acetate, the precipitate is obtained of full-metallic phosphate exclusively:

$$3FeSO_4 + 2Na_2HPO_4 + 2NaC_2H_3O_2 = Fe_3(PO_4)_2 + 3Na_2SO_4 + 2HC_2H_3O_2$$

178. Cyanides—as **KCy**—give a yellowish-red precipitate, chiefly ferrous cyanide, soluble in excess of the reagent; the solution constituting potassium ferrocyanide (compare 621).

Ferrocyanides—as K_4FeCy_6—precipitate *potassium-ferrous ferrocyanide*, $K_2FeFeCy_6$ (Everitt's salt), bluish-white, insoluble in acids. This is converted to Prussian blue (189), gradually by exposure to the air, immediately by oxidizing agents:

$$4K_2FeFeCy_6 + 2O + 4HCl = Fe_4(FeCy_6)_3 + K_4FeCy_6 + 4KCl + 2H_2O$$

Ferricyanides—as K_3FeCy_6—precipitate (even from dilute solutions) *ferrous ferricyanide*, $Fe_3(FeCy_6)_2$, dark blue, insoluble in acids. *This important test reveals the presence of traces of ferrous salt, in ferric solutions.* For this purpose, the solution must be dilute, as stated at 189, and the *original solution* always employed, because the oxidation of iron is altered by chemical operations.

Alkali hydrates decompose the precipitates above named: with potassium ferrous ferrocyanide, forming alkali ferrocyanide and ferrous hydrate· with ferrous ferricyanide, forming alkali ferricyanide and ferrous hydrate:

$$K_2FeFeCy_6 + 2KOH = K_4FeCy_6 + Fe(OH)_2$$
$$Fe_3(FeCy_6)_2 + 6KOH = 2K_3FeCy_6 + 3Fe(OH)_2$$

Sulphocyanates give no reaction with ferrous salts.

179. Oxalic acid and **oxalates** precipitate **ferrous oxalate**, FeC_2O_4, yellowish-white, crystalline, sparingly soluble in boiling water, decomposed by mineral acids not too dilute.

180. Tannic acid, and tincture of galls, with *concentrated* solutions of purely ferrous salts, give a white gelatinous precipitate of ferrous tannate, which is quickly oxidized by exposure to the air to blue-black ferric tannate—long used for writing ink.

181. By **ignition,** and in **beads** before the oxidizing flame of the blowpipe, ferrous compounds give the same reactions as ferric (192).

182. FERRIC salts form solutions having a brownish yellow **color,** and reddening **litmus.** Most soluble ferric salts are **deliquescent.** Ferric *oxide,* in powder, is reddish brown; in native crystal, steel-gray. It is soluble in hydrochloric acid, not very readily, but much quicker than in other acids.

183. The *hydrate,* oxalate, *phosphate, ferrocyanide, tannate,* gallate, borate, and sulphite, are **insoluble** in water. The chloride is soluble in *alcohol* and in *ether;* the sulphate is soluble in alcohol, a separation from ferrous sulphate. Ferric carbonate is not formed, and ferric sulphide is not formed in ordinary conditions of wet analysis. In **analysis,** ferric compounds are identified by the red solution they form with sulphocyanate, and distinguished from ferrous forms by not causing a blue precipitate with ferricyanide (189). Ferricum is separated in the First Division of Group III., with the other pseudo-triads (135).

184. The **alkali hydrates** precipitate *ferric hydrate,* $Fe_2(OH)_6$, variable to $Fe_2O_2(OH)_2$, reddish-brown, insoluble in alkalies or ammonium salts. Salts of fixed alkalies adhere to this precipitate with great tenacity.

185. Alkali **carbonates**—as K_2CO_3—also precipitate the hydrate, containing traces of carbonate (compare 147). Regarding barium carbonate, see 191.

$$Fe_2Cl_6 + 3K_2CO_3 + 3H_2O = Fe_2(OH)_6 + 6KCl + 3CO_2$$

186. Hydrosulphuric acid does not precipitate iron from ferric solutions; but reduces them to the ferrous combination, with precipitation of sulphur, as given in 171 *a.*

187. Ammonium sulphide precipitates the *ferrous sulphide* with free sulphur, **FeS** with **S,** a reduction of the metal to the condition of a dyad. Hence, the ammonium sulphide precipitate contains iron in ferrous condition only.

188. Phosphates—as Na_2HPO_4—precipitate *ferric phosphate,* $Fe_2(PO_4)_2$, scarcely at all soluble in acetic acid, but readily soluble in hydrochloric, nitric, and sulphuric acids. Hence, ferric salts which are not acetates, are precipitated by phosphoric acid with co-operation of alkali acetates (compare 177):

$$Fe_2Cl_6 + 2H_3PO_4 + 6NaC_2H_3O_2 = Fe_2(PO_4)_2 + 6NaCl + 6HC_2H_3O_2$$

In this way, phosphoric acid is removed from alkaline earth bases—in solutions of alkaline earth phosphates, in hydrochloric or nitric acid. Regarding precipitation by Arseniates, see 392.

189. Soluble **cyanides**—as **KCy**—precipitate, from ferric salts, the *hydrate,* with evolution of hydrocyanic acid (*a*).

Ferrocyanides—as K_4FeCy_6—precipitate *ferric ferrocyanide,* $Fe_4(FeCy_6)_3$, Prussian blue, insoluble in acids, decomposed by alkalies (*b*). Strong acids color the reagent blue, and render the test fallacious; acetic acid is free

from this objection, and addition of potassium acetate enables the test to be made in acid solutions. By excess of the reagent, the precipitate is somewhat soluble to a blue liquid.

Sulphocyanates—as **KCyS**—form, in solution, *ferric sulphocyanate*, $Fe_2(CyS)_6$, of a blood-red color so intense that this is an exceedingly delicate test for iron when in the ferric condition (*c*).

The red salt is freely soluble in water, alcohol, and ether, and extracted by ether from aqueous solutions; is decomposed by alkalies, but not by acids. Traces of ferric salts are revealed by adding the reagent, slightly over-saturating the mixture with **ether**; the excess of which will rise to the surface, colored by any ferric sulphocyanate, concentrated from the mixture.* The color of the liquid is destroyed by mercuric chloride (*d*); also by phosphates, borates, acetates, oxalates, tartrates, racemates, malates, citrates, succinates, and the acids of these salts. Molybdenum dioxide, also nitric and chloric acids, give red color with the sulphocyanate, removed by heat (643). To determine the condition of iron, *the original solution* only can be used (169).

Ferricyanides—as K_3FeCy_6—form *no precipitate* in ferric solutions, but give a green, or, in some proportions, brown color to the liquid (*e*), which should be *diluted* until transparent enough to reveal minute portions of blue precipitate if ferrous salt is present (178). The addition of *stannous chloride*, $SnCl_2$, or some other strong deoxidizing agent (171) to the mixture of ferricyanide, wherein no precipitate is found, constitutes a delicate test for ferric salts.

Some of the above-named reactions of ferric salts with cyanogen compounds, are defined in the following equations:

a. $Fe_2Cl_6 + 6KCy + 6H_2O = Fe_2(OH)_6 + 6HCy + 6KCl$

b. $Fe_4(FeCy_6)_3 + 12KOH = 3K_4FeCy_6 + 2Fe_2(OH)_6$

(Decomposition of K_4FeCy_6 by acids, see 627.)

c. $Fe_2Cl_6 + 6KCyS = Fe_2(CyS)_6 + 6KCl$ (Consult 19.)

d. $Fe_2(CyS)_6 + 3HgCl_2 = 3Hg(CyS)_2 + Fe_2Cl_6$

e. $Fe_2Cl_6 + 2K_3FeCy_6 = 6KCl + Fe_2(FeCy_6)_2$

190. The **acetates**—as $NaC_2H_3O_2$—form, in the cold, a dull red liquid, ferric acetate, $Fe_2(C_2H_3O_2)_6$, not decolorized by mercuric chloride. On boiling the solution, basic ferric acetate is precipitated, finally becoming hydrate. **Sulphites** give, likewise, a red solution of ferric sulphite, decomposed by boiling.†

191. Tannic acid—and tincture of galls—precipitate ferric salts blue-black, as ferric tannate, the basis of common ink.

* NATANSON, *Zeitsch. analyt. Chem.*, iii. 370.

† Meconic acid and Formic acid form red solutions *with ferric salts*. Benzoic acid gives a flesh-colored precipitate; salicylic acid a deep violet color; phenol and creosote, each a blue color; saligenin a blue color; and various compounds of the "aromatic group," hydroxyl substitutions in benzine derivatives, give blue to violet colors. Morphine, pseudomorphine, and daphnin, give the blue color.

Ammonium Succinate precipitates reddish-brown ferric succinate.

Barium Carbonate precipitates ferric hydrate from the chloride even in the cold (leaving barium chloride in solution):

$$Fe_2Cl_6 + 3BaCO_3 + 3H_2O = Fe_2(OH)_6 + 3BaCl_2 + 3CO_2$$

The excess of the barium carbonate is filtered out with the ferric hydrate, and may be separated by addition of sulphuric acid, which changes it to insoluble barium sulphate, and leaves ferric sulphate in solution. If ferrous chloride were in the original solution, the barium chloride formed in the reaction may be separated from it, likewise, by addition of sulphuric acid.

192. The larger number of iron salts are decomposed, as solids, by **heat**; ferric chloride vaporizes, undecomposed, at a very little above 100° C. (212° F.) **Ignition** in the air changes ferrous compounds, and ignition on charcoal or by the reducing flame changes ferric compounds to the *magnetic oxide*, which is attracted to the magnet.

In the outer **flame**, the **borax bead**, when moderately saturated with any compound of iron, acquires a reddish color while hot, fading and becoming light *yellow* when cold, or colorless, if feebly saturated. The same bead, held persistently in the *reducing* flame, becomes colorless unless strongly saturated, when it shows the pale *green* color of ferrous compounds. The reactions with **microcosmic salt** are less distinct, but similar. Cobalt, nickel, chromium, and copper conceal the reaction of iron in the bead.

Ferric compounds, heated briefly in a **blue borax bead** holding a very little **cupric oxide**, leave the bead blue; ferrous compounds so treated change the blue bead to red—the color of cuprous oxide.

193. Recapitulation of Distinctions between Ferric and Ferrous Compounds:

	Ferric compounds.	*Ferrous compounds.*
(1) Ferricyanides.	No. pre., green color, 189.	Deep blue pre. $Fe_3(FeCy_6)_2$.
(2) Sulphocyanates.	Red sol. $Fe_2(CyS)_6$.	No change.
(3) Ferrocyanides.	Blue pre. $Fe_4(FeCy_6)_3$.	Pale blue pre. $K_2FeFeCy_6$.
(4) Carbonates.	Effervescence (185).	No effervescence (175).
(5) Cyanides.	189.	178.
(6) Reducing Agents.		
Hydrosulph. acid.	171 *a*. (Deodorized and S. precipitated.)	
Sulphurous acid.	171 *b*. (Deodorized.)	
(7) Oxidizing Agents.		
Nitric acid,		814 (Brown gas, by heat.)
Bromine,		170 *b*. (Deodorized.)
Chlorine water,		170 *a*. (Deodorized.)

MANGANESE.

194. A grayish-white, hard, brittle, feebly magnetic **Metal**, difficult of fusion and of reduction, quickly oxidizing in the air, and even decomposing water at ordinary temperatures to a slight extent.

It accompanies iron in the mineral, vegetable, and animal kingdoms ; and artificial compounds of manganese are seldom free from iron, owing to the difficulty of complete separation.

195. Manganous Oxide, $Mn''O$, represents the only base capable of forming stable salts of manganese.

196. Manganic Oxide, $Mn''''_2{}^{VI}O_3$, represents a class of salts and compounds, all of which are *reduced to manganous combination by boiling with hydrochloric acid*, chlorine being evolved :

$$Mn_2Cl_6 \text{ (in boiling solution)} = 2MnCl_2 + Cl_2$$

For reactions of manganic compounds, see 213.

197. Manganese Dioxide, $Mn''''O_2$, constitutes the commercial source of manganese and an important oxidizing agent, as Pyrolusite. Salts of this type are not formed, and the action of hydrochloric acid with heat slowly dissolves (**reduces**) the dioxide to manganous chloride, with evolution of chlorine :

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$

Free chlorine, bromine, and iodine are obtained in accordance with this reaction (or some modification of it), and immense quantities of native manganese dioxide are required for the liberation of these elements, in manufacturing operations. The production of chlorine is frequently effected by using sulphuric acid and common salt, instead of hydrochloric acid :

$$MnO_2 + 2NaCl + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + Cl_2 + 2H_2O$$

Oxygen also can be obtained from binoxide of manganese, by action of sulphuric acid:

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O$$

Further, regarding Mn'''' as an oxidizing agent, see 848.

198. Manganic Acid is not known as such, but is represented in **manganates** ($K_2Mn^{VI}O_4$); those of the alkali metals being soluble in water, *with gradual decomposition* into manganese dioxide and permanganates :

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH$$

Free alkali retards, and free acids and boiling promote this change. Manganates have a green **color**, which turns to the red of permanganates during the decomposition inevitable in solution.

199. Permanganic Acid is not in use as an acid, but is represented by the permanganates, as $K_2Mn^{VIII}{}_2{}^{XIV}O_8$.* The permanganic acid radical is at once decomposed by addition of strong acids to a solid permanganate, but in water solution this decomposition

* In permanganates, manganese may be considered as an octad, in the compounds of which two of its atoms are held to each other by one bond of each ; the pair having twice seven bonds for other elements, and having always an even number of atoms in correctly written formulæ. But to avoid complexity of expression, in this work, permanganates will be written with an uneven number of atoms in the molecule.

does not at once take place, except by contact with oxidizable substances. The oxidizing power of permanganates extends to a great number of substances, possesses different characteristics in acid and in alkaline solutions, acts in many cases so rapidly as to be violently explosive, and is of such quantity that four parts of the absolute potassium salt furnish over one part of oxygen (equation *a*).

For the study of Permanganates in oxidation, see 849. The reactions with **ferrous salts** (*b*), and with oxalic acid (*c*), are much used in volumetric analysis :

a. $2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5O + 3H_2O$

b. $2KMnO_4 + 10FeCl_2 + 16HCl = 2MnCl_2 + 2KCl + 5Fe_2Cl_6 + 8H_2O$

c. $2KMnO_4 + 5H_2C_2O_4 + 6HCl = 2MnCl_2 + 8H_2O + 10CO_2 + 2KCl$

200. Permanganates are all **soluble** in water, silver permanganate being only sparingly soluble. The most of them are **deliquescent.** Their solutions have a deep red **color.** Slight deoxidation may give the green color of manganate.

201. Manganese is reduced to the manganous condition, from all its other degrees of combination, by boiling with hydrochloric acid. In this, its only stable form, it is most perfectly **identified as manganese**, and the various reactions of (*a*) the manganous base in the wet way obtained—202 and after.

b. For reactions characteristic of the **manganic base,** see 213 and after.

c. If the substance be a black powder, insoluble in water, but dissolving to manganous chloride in hydrochloric acid, with evolution of chlorine even in the cold (197), it is **manganese dioxide.** The proportion of absolute dioxide is determined from the amount of chlorine it is capable of setting free.

d. If having a green color (198), and being soluble in water with decomposition, etc., leaving manganous base, it is a **manganate,** representing manganic acid.

e. If soluble in water to a red color, and, by deoxidation, losing color (and leaving manganous base), it is indicated as a **permanganate** (199), representing permanganic acid.

202. MANGANOUS SALTS (195) are of rose **color.** The oxide is grayish-green. The chloride (4 *aq.*), bromide, iodide, and nitrate, are **deliquescent;** the sulphate (7 *aq.*) is efflorescent.

203. Manganous oxide, *hydrate, sulphide, carbonate, phosphate,* oxalate, borate, and sulphite, are **insoluble** in water. The *hydrate* is insoluble in alkalies, but soluble in solution of ammonium salts.

In **analysis,** manganese is identified by the oxidation of manganous hydrate or oxide, to manganate (211) or permanganate (210), each recognized by its bright color. As to determination of the oxidation of manganese, see 201.

204. The **alkali hydrates** precipitate, from soluble manganous salts, *manganous hydrate,* $Mn(OH)_2$, white, soon turning brown in the air by oxidation to *manganic oxyhydrate,* $Mn_2O_2(OH)_2$.

The precipitate is insoluble in excess of alkali, but—before oxidation—is soluble in solution of **ammonium salts,** by formation of soluble double salts of ammonium and manganese—ammonio-manganous salts—(corresponding to those of ammonium and magnesium ; compare 114). And hence, **ammonium hydrate** precipitates but part of the manganese in solution, forming in the reaction a salt of ammonium, which holds the rest of the manganese from precipitation.

The *manganic hydrate* is not only insoluble in ammonium salts but it is formed and precipitated from the ammoniacal solution of manganous hydrate in salts of ammonium by action of the air. After standing, all the manganese is so precipitated, dark brown; this precipitation by action of the air upon solution in ammonium salt being peculiar to manganese. As free ammonia facilitates the oxidation of metallic copper and of cobaltous salts, it may here promote the oxidation of the manganous compounds; also, it neutralizes the acid which would otherwise be set free.

205. Hydrosulphuric acid precipitates manganous acetate but imperfectly, and not in presence of acetic acid, and does not precipitate other salts, as manganous sulphide is soluble in very dilute acids, even acetic acid. **Ammonium sulphide** precipitates from neutral solutions, and forms from the recent hydrate of mixtures made alkaline, the flesh-colored *manganous sulphide*, **MnS**. Acetic acid, acting on the precipitated sulphides, separates manganese from cobalt and nickel, and from the greater part of zinc.

206. Alkali **carbonates** precipitate *manganous carbonate*, $MnCO_3$, white, oxidized by the atmosphere to the brown manganic hydrate (204), and, before oxidation, somewhat soluble in solution of ammonium chloride.

207. Alkali **phosphates**—as Na_2HPO_4—precipitate, from neutral solutions of manganous salts, normal *manganous phosphate*, $Mn_3(PO_4)_2$, white, slightly soluble in water, and soluble in dilute acids. It turns brown in the air.

The manganous hydrogen phosphate—$MnHPO_4$—is more soluble in water, and is obtained by crystallization from a mixture of manganous sulphate acidulated with acetic acid, and disodium hydrogen phosphate, Na_2HPO_4, added till a precipitate begins to form. From the **ammonio-manganese solution** (204), phosphates precipitate all the manganese as *ammonium-manganous phosphate.*

208. Alkaline **oxalates** precipitate *manganous oxalate*, soluble in acids not very dilute, and formed with difficulty by addition of oxalic acid.

209. Soluble **cyanides**—as **KCy**—precipitate *manganous cyanide*, $MnCy_2$, white, but darkening in the air, soluble in excess of the precipitant by formation of *double cyanides*—as $(KCy)_2MnCy_2$. This solution, exposed to the air, produces *manganicyanides*—analogous to ferricyanides—with oxidation of a portion of the manganese:

$$6(KCy)_2MnCy_2 + O_3 + H_2O = 4K_3MnCy_6 + Mn_2O_2(OH)_2$$

Ferrocyanides precipitate white *manganous ferrocyanide*, Mn_2FeCy_6, soluble in hydrochloric acid. **Ferricyanides** precipitate brown *manganous ferricyanide*, $Mn_3(FeCy_6)_2$, insoluble in acids.

210. Manganese is most easily and certainly identified through **oxidation**, by several methods, each method giving a *color-product.*

A small portion of manganous solution, when boiled with **nitric acid and lead dioxide**, is **oxidized** to *permanganic acid*, $HMnO_4$, giving a red color to the solution when the sediment subsides. The oxidation is derived from the lead dioxide, reduced to lead nitrate. If other reducing agents are present, they also must be oxidized. The lead dioxide should be used in such excess as to leave a black sediment.

211. Ignition with alkali and **oxidizing agents,** forming a *bright green* mass of alkaline *manganate,* constitutes a delicate and convenient test for manganese, in any combination. A small portion of precipitate or fine powder is taken. If the manganese forms but a small part of a mixture to be tested, it is better to submit the substance to the systematic course of analysis, and apply this test to the precipitate by alkali, in the third group. A convenient form of the test is by **ignition on platinum foil with potassium** or sodium **nitrate** and sodium carbonate (*a*). Ignition, by an **oxidizing flame,** on platinum foil, with potassium hydrate, effects the same result, less quickly and perfectly (*b*). Ignition by the oxidizing flame of the blow-pipe, in a **bead of sodium carbonate,** on the loop of platinum wire, also gives the green color (*c*).

a. $3Mn(OH)_2 + 4KNO_3 + Na_2CO_3 = 2K_2MnO_4 + Na_2MnO_4 + 4NO + CO_2 + 3H_2O$

b. $Mn(OH)_2 + 2KOH + 2O = K_2MnO_4 + 2H_2O$

c. $Mn(OH)_2 + Na_2CO_3 + 2O = Na_2MnO_4 + H_2O + CO_2$

212. With **beads of borax** and **microcosmic salt,** before the outer blow-pipe flame, manganese colors the bead violet while hot, and *amethyst-red* when cold. The color is due to the formation of *manganic oxide,* the coloring material of the amethyst and other minerals, and is slowly destroyed by application of the inner flame, which reduces the manganic to manganous oxide.

213. MANGANIC SALTS (196) are somewhat instable compounds, of a reddish-brown or purple-red **color,** becoming paler and of lighter tint in reduction to the manganous combination. The chloride and sulphate are **deliquescent.** Manganic **chloride,** Mn_2Cl_6, exists only in solution, which is *reduced* to $MnCl_2$ by boiling, also by evaporation to a solid. Manganic **sulphate**—$Mn_2(SO_4)_3$—is soluble in dilute sulphuric acid, but is reduced to $MnSO_4$ by the attempt to dissolve it in water alone ; potassium manganic sulphate and other **manganic alums** are also decomposed by water.

214. Hydrosulphuric acid *reduces* manganic salts to the manganous combination, with precipitation of sulphur. **Ammonium sulphide** reduces manganic chloride, and precipitates *manganous sulphide*—**MnS**—with free sulphur. **Alkali hydrates, carbonates,** and **barium carbonate,** all precipitate from solution of manganic chloride, *manganic hydrate,* $Mn_2O_2(OH)_2$. **Ferrocyanides** precipitate gray-green *manganic ferrocyanide,* $Mn_4(FeCy_6)_3$. **Ferricyanides** precipitate *manganic ferricyanide*—$MnFeCy_6$—brown. When a manganic compound is mixed with aqueous **phosphoric acid,** the solution evaporated to dryness and gently ignited, a violet or deep blue mass is obtained, from which water dissolves a purple-red *manganic hydrogen phosphate,* a distinction from manganous compounds. Simple **ignition** changes manganic compounds to Mn_3O_4. In the **tests in the dry way,** manganic compounds give the same reactions as manganous oxide (211).

COBALT.

215. Somewhat easier of reduction from oxides, and more fusible, than iron. The **metal** decomposes water at a red heat, but is permanent in the air at ordinary tempera-

tures. It is slowly dissolved by hydrochloric and sulphuric acids, with evolution of hydrogen—more promptly by nitric acid ; in each case forming cobaltous salt.

216. Cobalt forms two well-marked oxides (131), both of which represent bases in corresponding **classes of salts** : **cobaltous** salts, being stable compounds, permanent in the air, not easily affected by oxidizing agents ; **cobaltic** salts, very instable compounds, not permanent in solution, and easily reduced by heat alone to cobaltous combination. Therefore, as regards the relative stability of its two classes of compounds, cobalt, like manganese, is the reverse of iron. The most permanent cobaltic compound is the oxide; but both cobaltous and cobaltic oxides are changed, by ignition in the air, to cobaltoso-cobaltic or black oxide, Co_3O_4.

217. Cobaltous oxide is gray-green, the hydrate is rose-red ; they are easily soluble in acids forming **COBALTOUS SALTS**, which exhibit bright **colors**, *varied* by different physical states, and by different chemical combinations. In crystals, they are red ; anhydrous, mostly lilac. Their solutions are mostly blue when concentrated, but pink when diluted. At a certain stage of dilution, these solutions are red when cold, and blue when hot. The pink dilute solution of the chloride spreads colorless on white paper when cold, becomes blue on heating, and colorless when cold again, used as "*sympathetic ink.*" Cobaltous oxide dissolves in melted glass, coloring it blue—used to cut off the light of yellow flames (44) ; also, with the same color, in fused borax—the most delicate test for cobalt (224), and in other vitreous substances. The black, cobaltoso-cobaltic oxide, Co_3O_4—as left by ignition of cobaltous oxide or nitrate—combines or mixes, by ignition, with zinc oxide from zinc compounds to form a green mass, with aluminium compounds to a blue, and with magnesium compounds to a pink mass (blow-pipe tests for these metals, 119, 150, 240). Cobalt forms many double salts, and compounds with alkalies, noted for their various bright colors.

Cobaltous nitrate and acetate are **deliquescent** ; chloride, hygroscopic ; sulphate (7 *aq.*), efflorescent. The chloride **vaporizes**, undecomposed, at a high temperature.

218. The hydrate, basic carbonate, sulphide, phosphate, borate, oxalate, cyanide, ferrocyanide, and ferricyanide, are **insoluble** in water ; the potassio-cobaltous oxide is insoluble ; the ammonio-cobaltous oxide, soluble ; the double cyanides of cobalt and the alkali metals are soluble in water. Alcohol dissolves the chloride and nitrate ; ether dissolves the chloride, sparingly. Most of the salts insoluble in water form soluble compounds with ammonia. In **analysis**, cobalt is pretty clearly identified in the dry way, by the bead test (224). It is easily separated (221 and 244); except from nickel (223).

219. The **fixed alkalies** precipitate, from solutions of cobaltous salts, blue *basic salts*, which absorb oxygen from the air and turn olive-green, as cobaltoso-cobaltic hydrate, or if boiled before oxidation in the air, become rose-red, as *cobaltous hydrate*, $Co(OH)_2$. This last result is favored by excess of the reagent, which does not redissolve the precipitate. But ammonia and ammonium salts dissolve the precipitate.

Ammonium hydrate causes the same precipitate as fixed alkalies; incomplete, even at first, because of its solubility in the ammonium salt formed in the reaction, and soluble in excess of the ammonia to a solution which turns brown in the air by combination with oxygen, and is not precipitated by potassium hydrate. The reaction of the precipitate with ammonium salts forms a soluble double chloride (as with magnesium) ; the reaction of the precipitate with ammonia produces, in different conditions, different soluble color compounds, ammonio-cobaltous and ammonio-cobaltic, as $(NH_3)_4CoCl_2$, $(NH_3)_6CoCl_2$, $(NH_3)_8Co_2Cl_6$, etc.

220. Alkali **carbonates** precipitate *cobaltous basic-carbonate*, peach-red, which when boiled loses carbonic anhydride and acquires a violet, or, if the reagent be in excess, a blue color. The precipitate is soluble in ammonium carbonate (or in excess of that precipitant), and very slightly soluble in fixed alkali carbonates.

Barium carbonate does not precipitate cobaltous salts in the cold (except the sulphate), but by prolonged boiling does precipitate cobaltous chloride completely.

221. Hydrosulphuric acid, with normal cobaltous salts, gradually and imperfectly precipitates the black *cobalt sulphide*, **CoS**; from cobalt acetate, the precipitation is more prompt, and is complete ; but in presence of mineral acids, as in the second-group precipitation, no precipitate is made. When formed, the precipitate is scarcely at all soluble in dilute hydrochloric acid or in acetic acid ; slowly soluble in moderately concentrated hydrochloric acid, as in dissolving the third-group precipitate ; readily soluble in nitric, and most easily in nitro-hydrochloric acids. By exposure to the air, the recent cobaltous sulphide is gradually or slowly oxidized to cobalt sulphate, soluble, as occurs with iron sulphide, 176. **Ammonium sulphide** precipitates immediately and perfectly the black **CoS**, described above.

222. Phosphates—as Na_2HPO_4—precipitate the reddish *cobaltous phosphate*, $CoHPO_4$, soluble in acids and in ammonia. Oxalic acid and **oxalates** precipitate the reddish white, *cobaltous oxalate*, CoC_2O_4, soluble in mineral acids and in ammonia.

223. Alkali **cyanides**—as **KCy**—precipitate the brownish-white *cobaltous cyanide*, $CoCy_2$, soluble in hydrochloric, not in acetic or in hydrocyanic acid, soluble in excess of the reagent, as double cyanides of cobalt and alkali metals—$(KCy)_2CoCy_2$—potassium cobaltous cyanide, etc., the solution having a brown color :

$$CoCl_2 + 2KCy = CoCy_2 + 2KCl$$
$$CoCy_2 + 2KCy = (KCy)_2CoCy_2$$

Dilute **acids**, *without digestion*, reprecipitate cobaltous cyanide from this solution (the same as with nickel, 229) :

$$(KCy)_2CoCy_2 + 2HCl = CoCy_2 + 2HCy + 2KCl$$

But if the solution, with excess of the alkali cyanide and with a drop or two of hydrochloric acid, ensuring free **HCy**, be now *digested* hot for some time, the cobaltous cyanide is oxidized and converted into alkali *cobalticyanide*—as K_3CoCy_6—corresponding to ferricyanides, *but having no corresponding nickel compound :*

$$2CoCy_2 + 2HCy + O = Co_2Cy_6 \text{ (cobaltic cyanide)} + H_2O$$
$$Co_2Cy_6 + 6KCy = 2K_3CoCy_6, \text{ potassium cobalticyanide.}$$

In the latter solution acids cause no precipitate (compare 229)—(*important distinction from nickel*, whose solution remains $(KCy)_2NiCy_2$, and after digestion as above is precipitated with acids).

Sulphocyanate, in highly concentrated solution, gives *a blue color*, $Co(CyS)_2$, crystallizable in blue needles, soluble in alcohol, not in carbon disulphide. In less concentrated solutions, the color appears on warming. In neutral solutions, nickel, iron, manganese, and zinc, do not interfere (Schoenn, 1870).

Ferrocyanides—as K_4FeCy_6—precipitate *cobaltous ferrocyanide*, Co_2FeCy_6, gray-green, insoluble in acids. **Ferricyanides**—as K_3FeCy_6—precipitate *cobaltous ferricyanide*, $Co_3(FeCy_6)_2$, brownish-red, insoluble in acids. But a more distinctive test is made by adding **ammonium chloride** and **hydrate**, with the ferricyanide, when *a blood-red color* is obtained, in evidence of cobalt. If, in this test, manganese be present, a white precipitate is obtained at once, becoming brown with more ferricyanide ; if nickel be present, a copper-red precipitate forms on boiling ; zinc gives no precipitate, hot or cold, but on addition of ferrocyanide to the same solution, gives a white precipitate (Allen, 1871).

224. In the bead of borax, and in that of microcosmic salt, with oxidizing and with

reducing flames, cobalt gives an intense *blue* color. The blue bead of copper changes to brown in the reducing flame. If strongly saturated, the bead may appear black from intensity of color, but will give a blue powder. This important test is most delicate with the borax bead (217). If sulphur or arsenic is present, it must be previously expelled by roasting. If manganese, copper, nickel, or iron is present, the continued application of the *reducing* flame will destroy the interfering color, and bring out the blue of cobalt.

By **ignition**, with sodium carbonate on charcoal or with the reducing flame, compounds of cobalt are reduced to a *magnetic mass.*

225. Cobaltous compounds are **oxidized to cobaltic** combinations, in the following tests, all of which distinguish cobalt from nickel, which is scarcely capable of higher oxidation.

Potassium nitrite, KNO_2, added to a somewhat concentrated solution of cobaltous salt, with addition of sufficient acetic acid, after warm digestion, on standing some time, better for twenty-four hours, causes a yellow crystalline precipitate of *potassium cobaltic nitrite* (a separation from nickel):

$$2CoCl_2 + 12KNO_2 + 2HC_2H_3O_2 + H_2O = (KNO_2)_6, Co_2O(NO_2)_4, (H_2O)_2 + 4KCl + 2KC_2H_3O_2 + 2NO$$

Chlorine gas, passed into dilute cobaltous solutions, changes them to cobaltic combinations, which are then precipitated by digestion with **barium carbonate** in the cold (compare 220). **Lead dioxide**, with warm digestion, precipitates from neutral solutions all the cobalt, as *cobaltic oxy-hydrate.*

NICKEL.

226. In the properties of nearly all its compounds, this metal closely *resembles cobalt;* so that its analysis requires a constant comparison between the reactions of the two metals; and although it is not difficult to identify the one in the presence of the other, their exact separation is laborious.

The **metal** is reduced from its oxide, and is oxidized by ignition in the air, about as readily as iron, but at ordinary temperatures is less easily oxidized in the air, having a silver-white, brilliant lustre, and is a little more fusible than iron. In reduction with carbon, it forms a carbide, like iron. It is slowly dissolved by dilute hydrochloric or sulphuric acid with evolution of hydrogen, and readily by nitric acid or chlorine water.

Nickel forms two oxides—protoxide, or nickelous oxide, $Ni''O$, gray-green, representing the **salts** of nickel, and nickelic oxide, $Ni_2^{VI}O_3$, not salifiable. Both oxides readily dissolve in acids, as nickelous salts.

227. The salts of nickel have a delicate green **color** in crystals and in solution; when anhydrous, they are yellow. The nitrate and chloride are **deliquescent** or **efflorescent**, according to the hygrometric state of the atmosphere; the acetate is efflorescent. The chloride **vaporizes** at high temperatures.

The hydrate, carbonate, sulphide, phosphate, borate, oxalate, cyanide, ferrocyanide, ferricyanide, **insoluble** in water. The compounds of the oxide with potassium oxide and sodium oxide are insoluble; that with ammonia is soluble; and the double cyanides of nickel and alkali metals are soluble in water. The chloride is soluble in alcohol, and the nitrate in dilute alcohol. Most salts of nickel form soluble compounds by action of ammonium hydrate. In **analysis** nickel is separated, with cobalt, by the sparing solubility of the sulphide in dilute acids. Its separation from cobalt is more difficult (229). In absence of cobalt, it is easily identified in the bead (231).

228. The **fixed alkali hydrates** precipitate *nickel hydrate*, $Ni(OH)_2$, pale green,

insoluble in excess of the reagent and not oxidizable in the air, but soluble in ammonium hydrate or ammonium salts to a greenish blue liquid (133).

Ammonium hydrate, also, precipitates nickel hydrate, soluble in excess, and in ammonium salts, with formation of compounds similar to those of cobalt (219), giving a violet blue color to the solution. Sufficient potassium or sodium hydrate will slowly reprecipitate nickel hydrate from its ammoniacal solution, a distinction from cobalt. In dilute ammoniacal solutions, the blue color appears only after exposure to the air.

The alkaline **carbonates** precipitate basic carbonate of variable composition, green color, and soluble in ammonium carbonate, or excess of that precipitant—with blue or greenish-blue color.

With **hydrosulphuric acid,** and with **sulphide of ammonium,** nickel has the same deportment as cobalt (221): the precipitate being *nickel sulphide,* slightly soluble in excess of ammonium sulphide. **Phosphates**—as Na_2HPO_4—throw down *nickel phosphate,* greenish-white, mostly full metallic.

229. Alkali **cyanides**—as **KCy**—precipitate *nickel cyanide,* $NiCy_2$, yellowish-green, insoluble in hydrocyanic acid, and in cold dilute hydrochloric acid; dissolving in excess of the cyanide, by formation of soluble double cyanides—as potassium-nickel cyanide, $(KCy)_2$-$NiCy_2$. The equation of the change corresponds exactly to that for *cobalt* (223); and the solution of double cyanide is reprecipitated as $NiCy_2$ by a careful addition of **acids** (like cobalt); but hot digestion, with the liberated hydrocyanic acid, forms no compound corresponding to cobalticyanides, and does not prevent precipitation by acids (unlike cobalt). It will be observed, that excess of hydrochloric or sulphuric acid will dissolve the precipitate of $NiCy_2$. **Ferrocyanides**—as K_4FeCy_6—precipitate a greenish-white *nickel ferrocyanide,* Ni_2FeCy_6, insoluble in acids, soluble in ammonium hydrate, decomposed by fixed alkalies. **Ferricyanides** precipitate greenish-yellow *nickel ferricyanide.*

For the test by ferricyanide, with ammonium chloride and hydrate, in distinction from *cobalt,* see 223.

Oxalic acid and **oxalates** precipitate, very slowly, but almost completely, after twenty-four hours, *nickel oxalate,* green.

230. Chlorine, or hypochlorite, in neutral solution or, better, with fixed alkali hydrate, forms a black precipitate of *nickelic hydrate,* $Ni_2(OH)_6$, reduced by heat or by solution in acids or in ammonium hydrate. The separation of nickel from cobalt (225), by this test, is more accurate if potassium cyanide in excess be added previously to the chlorine or hypochlorite. Nitrites, with acetic acid, do not oxidize nickel as they do cobalt.

231. Nickel compounds dissolve clear in the **borax bead,** giving with the oxidizing flame a purple-red or violet color while hot, becoming yellowish-brown when cold; with the reducing flame, fading to a turbid gray, from reduced metallic nickel, and finally becoming colorless. The addition of any potassium salt, as potassium nitrate, causes the borax bead to take a dark purple or blue color, clearest in the oxidizing flame. With **microcosmic salt,** nickel gives a reddish-brown bead, cooling to a pale reddish-yellow, the colors being alike in both flames. Hence, with this reagent, in the reducing flame, the color of nickel may be recognized in presence of *iron* and *manganese,* which are colorless in the reducing flame; but *cobalt* effectually obscures the bead-test for nickel. The yellow-red of *copper* in the reducing flame, persisting in beads of microcosmic salt, also masks the bead-test for nickel.

By **ignition** with soda on charcoal, compounds of nickel are reduced to a powder attracted by the *magnet.*

ZINC.

232. In general properties, zinc resembles magnesium and cadmium, all of which are volatile at about a red heat, their vapors oxidizing in the air, while their oxides are non-volatile. Zinc melts at 411° C. (773° F.)

233. *Pure* zinc **dissolves** very slowly in acids or alkalies, unless in contact with copper, platinum, or some less positive metal. The metallic impurities in ordinary zinc enable it to dissolve easily with acids or alkali hydrates. In contact with iron, it is quite rapidly oxidized in water containing air, but not dissolved by water, unless by aid of certain salts. All the agents which dissolve the metal, dissolve also its oxide and hydrate.

The metal dissolves in hydrochloric, sulphuric, and acetic acids (*a*), and in the aqueous alkalies (*b*)—with evolution of hydrogen; in very dilute nitric acid, without evolution of gas (*c*); in moderately dilute cold nitric acid, mostly with evolution of nitrous oxide (*d*); and, in somewhat less dilute nitric acid, chiefly with evolution of nitric oxide (*e*). Concentrated nitric acid dissolves zinc but slightly—the nitrate being very sparingly soluble in nitric acid:

a. $Zn + H_2SO_4 = ZnSO_4 + 2H$

b. $Zn + 2KOH = K_2OZnO + 2H$

c. $4Zn + 10HNO_3 = 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$

d. $4Zn + 10HNO_3 = 4Zn(NO_3)_2 + N_2O + 5H_2O$

e. $3Zn + 8HNO_3 = 3Zn(NO_3)_2 + 2NO + 4H_2O$

234. The *chloride*, bromide, iodide, chlorate, nitrate (6 *aq.*), and *acetate* (7 *aq.*) are **deliquescent**; the *sulphate* (7 *aq.*) is **efflorescent**.

The oxide, *hydrate, sulphide, basic carbonate*, phosphate, arseniate, oxalate, and ferrocyanide, are **insoluble** in water; the sulphite is sparingly soluble. Most salts of zinc, insoluble in water, form soluble compounds by action of any of the alkali hydrates.

Zinc is **separated** from the metals of the third group, except from aluminium, by non-precipitation with excess of fixed alkali hydrate in boiling solution; from aluminium, by precipitation as sulphide in alkali solution, and by non-precipitation with excess of ammonium hydrate (235).

235. The **alkali hydrates** all precipitate the *hydrate of zinc*, $Zn(OH)_2$, white, soluble in excess of either precipitant, with formation of potassium or sodium zinc oxide, or zincate, K_2ZnO_2, or $Zn(OK)_2$:

$ZnCl_2 + 2KOH = Zn(OH)_2 + 2KCl$

$Zn(OH)_2 + 2KOH = K_2ZnO_2 + 2H_2O$

On *boiling* the alkaline solutions, if dilute, a precipitate of zinc oxide separates, more readily from the ammonic than from potassic or sodic solutions. In the *presence of iron*, or manganese, the zinc hydrate does not so readily dissolve in the alkali precipitant, which in these cases needs to be very strong, at the time of precipitation.* Hydrate of zinc is somewhat soluble in ammonium chloride, as stated in 134.

236. Hydrosulphuric acid precipitates a *part* of the zinc from neutral solutions of its salts with mineral acids, and the whole from the acetate; also from other salts of zinc, if with addition of alkali acetates (separation from manganese):

$$ZnCl_2 + 2KC_2H_3O_2 + H_2S = ZnS + 2KCl + 2HC_2H_3O_2$$

That is: Zinc sulphide is not soluble in moderately dilute acetic acid, though much more soluble in mineral acids. The precipitate is *white* when pure.

237. Alkali **sulphides**—as $(NH_4)_2S$—completely precipitate zinc as *sulphide*, both from its salts with acids and from its soluble combinations with alkalies.

238. Alkali **carbonates**—as K_2CO_3—precipitate *basic carbonate*, white, $Zn_5(OH)_6(CO_3)_2$ sparingly soluble in ammonium carbonate, readily in ammonium hydrate.

239. Alkaline **cyanides**—as **KCy**—precipitate *zinc cyanide*, $ZnCy_2$, white, soluble in excess of the precipitant. Alkaline **ferrocyanides**—as K_4FeCy_6—precipitate zinc ferrocyanide, Zn_2FeCy_6, white. Alkaline **ferricyanides**—as K_3FeCy_6—precipitate zinc ferricyanide, $Zn_3(FeCy_6)_2$, yellowish.

* The solution of the zinc hydrate precipitate, by addition of excess of alkalies, is greatly affected by conditions of temperature and dilution. At 16° to 17° C., one c.c. of Normal standard solution of zinc sulphate requires, to redissolve the precipitate, eight c.c. of Normal standard solution of potassium hydrate. But now, just one-half of the alkali can be taken up, by adding four c.c of half-Normal solution of sulphuric acid, before the precipitate reappears. That is, four molecules of the alkali hydrate form and dissolve (or hold in a solution already made) the precipitate of one molecule of the zinc salt—supporting the equations in the text. But, if the equation is to represent the proportion of alkali necessary to add in order to make and dissolve the precipitate, at first, it must show eight molecules of alkali hydrate to one zinc salt, thus:

$$ZnSO_4 + 8KOH = Zn(OK)_2.4KOH + K_2SO_4 + 2H_2O$$

The addition of water, at a certain point, precipitates the alkali solution after it is made. Heat does the same, as stated in the text. At 50° C., about three times as much of the alkali solution is required to dissolve the precipitate, as at 17° C. The addition of an alkali solution so dilute as the tenth-Normal, in case of potassium hydrate, does not effect full solution of the precipitate, however much is added. Sodium hydrate solution is not required in quite so large excess to redissolve the precipitate—seven molecules being needed, in Normal solutions, instead of eight, as for potassium hydrate. But the same proportion of four molecules is needed to hold the solution, after taking up excess by adding acid. In the case of ammonium hydrate, 6.6 c.c. of Normal standard solution were found to be required to form and dissolve the precipitate from 1 c.c. of Normal solution of zinc salt. Then 1.6 c.c. of the alkali could be taken up by acid, before reprecipitation. Apparently, then, five molecules of ammonium hydrate are required for soluble combination with one molecule of zinc salt. [See a report on Zinc and Alkali solutions, by the author and F. L. Wilson, *Jour. Am. Chem. Soc.*, Feb., 1880, ii. 29.]

240. With sodium carbonate, on charcoal, before the **blow-pipe,** compounds of zinc are reduced to the metallic state. The metal is vaporized, and then oxidized in the air, and deposited as a non-volatile coating, *yellow when hot and white when cold* (compare 140). If this coating, or zinc oxide otherwise prepared, be moistened with solution of **cobalt nitrate** and again ignited, it assumes a *green* color.

With borax or microcosmic salt, zinc compounds give a **bead** which, if strongly saturated, is yellowish when hot, and opaque white when cold.

241. Comparison of some Reactions of Third Group Bases.

In Water Solution, as Chlorides, Nitrates, Sulphates, etc.

	Aluminium.	Chromium.*	Ferricum.	Ferrosum.	Manganese.	Cobalt.	Nickel.	Zinc.
KOH or NaOH	$Al_2(OH)_6$ †	$Cr_2(OH)_6$ ‡	$Fe_2(OH)_6$	$Fe(OH)_2$	$Mn(OH)_2$	$Co(OH)_2$	$Ni(OH)_2$	$Zn(OH)_2$†
NH_4OH	"	"	"	"	"	" ¶	" ¶	" ¶
NH_4OH with NH_4Cl	"	"	"	No pre.	No pre.	No pre.	No pre.	No pre.
Carbonates.	"	"	"	$FeCO_3$	$MnCO_3$	Basic Carb.	Basic Carb.	Basic Carb.
Sulphides.	"	"	FeS with S	FeS	MnS	CoS	NiS	ZnS
H_2S in acid. sol.	No pre.	(S) **	S **	No pre.	No pre.	††	††	††
Na_2HPO_4	$Al_2(PO_4)_2$ ‡‡	$Cr_2(PO_4)_2$ ‡‡	$Fe_2(PO_4)_2$ ‡‡	$FeHPO_4$(177)	$Mn_3(PO_4)_2$	$CoHPO_4$	$NiHPO_4$	$ZnHPO_4$
Oxidizing agents.		Base to acid.		To ferric.	Base to acid.	Cobalticum.		
Reducing agents.		Acid to base.	To ferrous.		Acid to base.			

* Chromic acid and its salts furnish Cr_2^{VI} as a base when treated with ammonium sulphide and other reducing agents (166 *d*.)
† The precipitates soluble in excess of the reagent (145, 235).
‡ The precipitate soluble in excess of the cold reagent, but thrown down again on boiling (154).
¶ The precipitates soluble in excess of the reagent (133).
** In case of chromates, the solution turns green with precipitation of S (166 *a*); in case of ferric salts, the color fades, with precipitate of S (171 *a*).
†† In solutions of normal acetates, hydrosulphuric acid gives precipitates (221, 228, 236).
‡‡ Much less soluble in acetic acid than alkaline-earth phosphates (188).

242. Separation of Third Group Metals by NH_4OH with NH_4Cl, etc. (Phosphates, Oxalates, etc., being absent.) (Explanation in 243.)

To the clear filtrate from Group II., in which H_2S will cause no precipitate, and freed from H_2S by boiling, add a few drops of **Nitric Acid** and boil an instant (to oxidize ferrosum.*) Immediately add **Ammonium Chloride** and excess (133) of **Ammonium Hydrate.** If there is a precipitate, filter and wash.

Precipitate, Group III. A: $Fe_2(OH)_6$, $Cr_2(OH)_6$, $Al_2(OH)_6$.

Pierce the point of the filter, and with a little water wash the precipitate into a test-tube; add **Potassium** or **Sodium Hydrate,** and boil for several minutes. If a residue remains, filter and wash.

Precipitate: $Fe_2(OH)_6$, $Cr_2(OH)_6$.

For Iron, dissolve the precipitate in a little diluted **hydrochloric acid**, and test the solution (for Fe_2Cl_6) with **potassium sulphocyanate** (189). If iron is present, this solution will give all the reactions of ferricum.

Iron being found, to determine whether it is ferric or ferrous, or both,† in the original solution, test the latter, according to 193.

Study the characteristics of iron by use of the Table of Comparisons on the preceding page, the recapitulation in 193, and the text upon iron throughout.

For Chromium, test a portion of the precipitate, by fusing on platinum foil with **sodium** or **potassium nitrate** and **carbonate,** to change to *chromate* (159 *d*). Dissolve the mass (Na_2CrO_4) in water; filter if necessary, and examine the clear, acidified solution for chromic acid, by 163–4–5.

Or oxidize by lead dioxide (159 *c*).

If the original solution contains Chromate, it also will give the reactions of chromic acid (163–4–5), and have a color mentioned in 161. If it contains *Chromic salt*—as $Cr_2(SO_4)_3$—it will give the reactions described in 154 and after.

Solution: $K_2Al_2O_4$.

For Aluminium, add to the potassium (or sodium) solution enough **hydrochloric acid** barely to acidulate it, and then add **ammonium carbonate.** A precipitate is $Al_2(OH)_6$. (The result is obtained with nearly equal certainty by addition of excess of **ammonium chloride** to the alkaline solution, 145.)

Study aluminium as indicated in the Table of Comparisons, and in the text at 141, and after.

* In the filtrate from the Second Group, iron is necessarily in the ferrous condition (186).

† Ferrous salts, which have been kept in the air, are never wholly free from ferric compounds (169).

Filtrate, Group III. B : Contains Zn, Ni, Co, Mn.

Add **Ammonium Sulphide,** and if a precipitate appears, warm until it subsides. Filter and wash. (This filtrate is to be examined for the Fourth Group, 798.)

Precipitate : ZnS, NiS, CoS, MnS.

Treat, on the filter, with cold dilute **Hydrochloric Acid.** Note if a black residue remains. Boil the filtrate.

Residue : NiS, CoS* (black).

For Cobalt, test the residue by the **blow-pipe** (224).

The residue may be dissolved in a very little nitro-hydrochloric acid, and treated for the reactions, stated in 223.

In the study of cobalt, verify the reactions noted in the Table of Comparison, and described in the text (217, and after).

For Nickel, test the residue by the **blow-pipe** (231).

Then obtain reactions in the wet way, and separation from cobalt, by dissolving the residue in a very little nitro-hydrochloric acid, and treating by 229, and the adjacent text. (Cobalt is removed by one of the methods in 225.)

Solution : $ZnCl_2$, $MnCl_2$.

Add a decided excess of **potassium** or **sodium hydrate,** and digest without warming. Filter.

Precipitate : $Mn(OH)_2$.*

Test *for manganese* by oxidations as by 210; 211, *a;* also, 212.

The precipitate may be dissolved with hydrochloric acid, for reactions (204 and after, and Table of Comparisons).

For acids of manganese, Mn_2^{VI} and Mn'''', examine the original material by aid of 201.

Solution : K_2ZnO_2.

Test *for zinc* by adding **ammonium Sulphide :** precipitate, **ZnS.**

The reactions of zinc salts are obtained from the alkaline solution after acidulating it.

Study the characteristics by aid of the Table of Comparisons, and the text at 235 and after.

* Small portions of cobalt and nickel may be dissolved from their sulphides by hydrochloric acid, and then will be precipitated with $Mn(OH)_2$. This precipitate may be tested for **Co** and **Ni** by the blow-pipe, as above directed.

242½. Thiosulphate Process for the Third Group.*

To the filtrate from the Second Group (or a solution containing no second group bases) add **Ammonium Hydrate** to an alkaline reaction, and then **Ammonium Sulphide** (136).

The **Precipitate** to be examined for **Cr, Al, Fe, Zn, Mn, Co, Ni.**

Dissolve the washed precipitate by **Hydrochloric Acid.** (If a black residue remains, dissolve it by nitro-hydrochloric acid.) To this solution (or an original solution of salts of third group metals only), add **Sodium Carbonate** till a slight precipitate is formed ; then add a few drops of **Bromine**, and boil, keeping the liquid neutral with sodium carbonate (159 *a*). Finally, add the latter in excess, and filter (138).

Solution :

Examine for **Cr.** Acidify with acetic acid, and test with lead salts, etc., 163.

Dissolve the washed **Precipitate** in the least possible quantity of **Hydrochloric Acid.** To the solution add **Sodium Carbonate** till a slight precipitate is formed ; then add a few drops of **Acetic Acid,** and, finally, **Sodium Acetate** in excess. Boil and filter (147, 190).

Precipitate :

Examine for **Al, Fe.**
Dissolve by **HCl,** neutralize with Na_2CO_3, then add **Sodium Thiosulphate** in excess. Boil for an hour or more, and filter (149).

Residue :	**Solution :**
Al, (as hydrate, or, if PO_4 be present, as phosphate, 149).	Test for **Fe** (here ferrous).

To the **Solution,** add **Sodium** (or **Potassium**) **Hydrate** in excess, warm gently, and filter (235).

Solution :

Test for **Zn,** by adding Ammonium Sulphide.

Dissolve the **Precipitate** with **HCl,** neutralize with **NaOH,** and add excess of $(NH_4)_2S$. Filter, and treat the precipitate with **Acetic Acid** (205).

Solution :

Test for **Mn,** by evap., and fusing residue with nitrate and alkali, 211 *a*.

Residue : Dissolve in HNO_3, evap. to dr. on water-bath, add water, then KNO_2, then Acetic Acid in excess. Warm and let stand 24 hrs. (225).

Residue :	**Solution :**
Co. Test, 224.	Test for **Ni,** 231.

* For the scheme of separations here tabulated, the author is indebted altogether to Professor Henry A. Weber, Ph.D., who has used it, as a working plan, for some time, in the Laboratory of the Illinois Industrial University. The title "Thiosulphate Process" is here adopted, from the aluminium-iron separation, Chancel's method.

SEPARATION OF THE THIRD GROUP METALS.

243. The reactions of the seven important metals of the third group, as obtained with the compounds of each alone, include a sufficient number of distinct differences to construct several easy methods of complete separation. But it is more difficult to separate them when together than to distinguish them when apart, owing to the fact that the reactions of several of them are modified by the presence or action of others. In some of these cases, the interference is probably due to simple adhesion between the bases; in others, to chemical action of one base with another.

The division of the third group, by action of **ammonium chloride,** which dissolves manganous hydrate, and excess of **ammonium hydrate,** which dissolves cobalt, nickel and zinc hydrates, is indicated in the Table of Comparison (241), and constitutes the first separation used in the Table at 242. If the excess of ammonium hydrate be decided, the solution of the cobalt, nickel, and zinc will not fail. To dissolve the manganese, the ammonium salt must be added abundantly, and the metal must be in the manganous condition (204). Hence the oxidation of ferrosum, by nitric acid, must be limited to addition of very little nitric acid with very brief boiling, to avoid the formation of manganic compounds.

The following precautions are essential to this method of separation: (*a*) All hydrosulphuric acid left from the second-group precipitation must be expelled. (*b*) Iron must be obtained in the ferric condition, as stated in the Table (242). (*c*) If citric and tartaric acids, sugar, albumen, and other organic substances which prevent precipitation by alkalies are present, they must be destroyed by evaporating the filtrate from the second group to dryness; adding a few drops of nitric acid, gently igniting, then dissolving in water acidulated with hydrochloric acid. A carbonaceous residue may be disregarded.

The separation of $Al_2(OH)_6$, from $Fe_2(OH)_6$, and $Cr_2(OH)_6$, by excess of fixed alkali, as directed in 242 A, requires that the alkali should be strong enough to dissolve the aluminium, and that the boiling should be sufficient to precipitate the chromium (154).

244. The separation of **CoS** and **NiS**, from the other sulphides of Group III. B, as directed in the Table at 242, is not complete, as has been stated in a foot-note of the table. If acetic acid be employed instead of hydrochloric acid as a solvent, **CoS** and **NiS** will be left in the residue without waste; but now the **ZnS** will chiefly remain undissolved (236 and 241, under H_2S). The separation of zinc from manganese can be done by treating their sulphides with acetic acid, as mentioned in the Table for "Anal. of Group III., when Phosphates are present," 797, also by treating their acetates with hydrosulphuric acid.

245. The following **Plan of Separation, chiefly by excess of alkali hydrates,** may be employed as a study :

Dissolve the third group (ammonium sulphide) precipitate *in hydrochloric acid with* a very little potassium *chlorate.*

In solution : $ZnCl_2$, Al_2Cl_6, Cr_2Cl_6, $MnCl_2$, Fe_2Cl_6, $CoCl_2$, $NiCl_2$.

Add ammonium chloride, then ammonium hydrate in decided *excess,* and filter and wash.

Residue (*a*): $Fe_2(OH)_6$, $Al_2(OH)_6$, $Cr_2(OH)_6$.

Solution (*b*): **ZnO, MnO, CoO, NiO** (as ammonio compounds).

Dissolve residue (*a*) *in hydrochloric acid ;* add *excess of potassium hydrate* in the cold. Filter.

Precipitate (*c*): $Fe_2(OH)_6$. (Dissolve in acid and test.)

Solution (*d*): $K_2Al_2O_4$, $Cr_2O_3(K_2O)_n$

Boil filtrate (*d*) for some time. Filter.

Precipitate (*e*): $Cr_2(OH)_6$. (Test by 159 *d*, etc.)

Solution (*f*): $K_2Al_2O_4$. (Acidulate and test, 145, etc.)

To solution (*b*)—

Add sulphide of ammonium ; filter and wash the precipitate formed. Digest with moderately dilute *hydrochloric acid in the cold,* and filter.

Residue (*g*): **CoS, NiS.** (Test 242, B.)

Filtrate (*h*): $ZnCl_2$, $MnCl_2$.

Boil *filtrate* (*h*) ; *add excess of potassium hydrate,* and filter.

Precipitate : $Mn(OH)_2$. (Test by 211, *a.*)

Solution : K_2ZnO_2. (Acidulate and test, 235, etc.)

In this plan—besides the difficulty with **manganese,** explained in 243—we have the difficult solution of **chromium** in cold, fixed alkali in presence of iron, and the uncertain solution of **aluminium** by alkali in presence of iron. Also, the separation of **cobalt** and **nickel,** both by redissolving in ammonium hydrate, and by non-solution of their sulphides in hydrochloric acid, are processes requiring care, and affording only approximate separation.

246. The presence of **Phosphoric Acid** greatly complicates the analysis of the third group. Hence, the first proceeding with the filtrate of the second group is to ascertain whether it contains phosphoric acid or not. This is most conclusively done, as directed in the Table for Grouping (793), by the test with molybdate. It will be remembered, however, that a solution containing phosphoric acid along with any non-alkali bases must have an acid reaction (708). As soon as the solution is neutralized, phosphates are precipitated, and so phosphates are thrown down in third group precipitations. As phosphoric is a non-volatile acid, it must be removed by precipitation. To separate it from bases, it must be precipitated from acid solution. This is done, *firstly,* as directed in the

Table for "Analysis of Group III. when Phosphates are present" (797), by adding excess of ferric chloride, and then barium carbonate, in a very slightly acid solution. The PO_4 is precipitated as ferric phosphate, with the other two pseudo-triads of the group, aluminium and chromium, both as hydrates. The phosphates of the pseudo-triads, especially ferric phosphate, are less easily dissolved by diluted acids or by acetic acid than any other metallic phosphates, except, perhaps, lead phosphate. In this way the dyad metals of the third and fourth groups are obtained in solution, free from PO_4, as they are not precipitated by barium carbonate. Now the precipitate of $Al_2(OH)_6$, $Cr_2(OH)_6$, $Fe_2(PO_4)_2$, etc., is boiled with excess of fixed alkali, which brings the aluminium into solution, $K_2Al_2O_4$, free from PO_4. The chromium is identified, in the very complex precipitate, by its oxidation to acid, and the color precipitates of chromate.

247. *Secondly*, the phosphoric acid radical can be separated from the alkaline earth-metals, and from the dyads of the third group, by ferric salt in presence of *acetic acid* (248). There must be no other free acid; the ferric phosphate itself being soluble in hydrochloric and other strong acids. The acetic acid must be strong enough to prevent the precipitation of phosphates of calcium, etc.; and when of this strength it does dissolve some ferric phosphate, so that the separation is not very close. Ferric chloride being taken as a reagent, sodium acetate is used, so that the chlorine shall be neutralized as metallic salt, and not appear as hydrochloric acid:

$$Fe_2Cl_6 + 6NaC_2H_3O_2 = Fe_2(C_2H_3O_2)_6 + 6NaCl$$

$$Fe_2Cl_6 + 6NaC_2H_3O_2 + 2H_3PO_4 = Fe_2(PO_4)_2 + 6NaCl + 6HC_2H_3O_2$$

In the following table this principle is employed, with certain precautions. Group III. A, is obtained by itself; then put with Group III. B, and digested with sulphide; because, it is claimed, in this way the phosphoric acid radical is combined with the pseudo-triads to a greater extent than when ammonium sulphide is brought to bear upon the whole group in solution. After the use of the sulphide, ferrosum may be present and again require oxidation, and the free chlorine used for this purpose also secures the solution of CoS and NiS. On digestion with *the acetate*, a precipitate must occur if Fe, Al, or Cr, is present. This precipitate may contain all these pseudo-triads, when it probably will not contain all the PO_4; or it may contain all the PO_4, when it probably will not contain all the pseudo-triads. To assure the removal of all the PO_4, ferric salt is added. The filtrate is now free from phosphoric acid, and is to be treated essentially as directed for the third group when phosphates are absent—obtaining precipitates of Group III. A and B, and carrying the filtrate to the fourth group.

248. Separation of Third and Fourth Group Metals and Phosphoric Acid from each other, by Use of Alkali Acetate. (Explanation in 247.)

To the clear filtrate from Group II., freed from H_2S by boiling, add a few drops of **nitric acid,** and boil an instant ; then at once precipitate by **ammonium chloride** and excess of **ammonium hydrate**. Filter, and precipitate by **ammonium sulphide** (as directed in 242). Filter, and reserve this filtrate for Group IV.* Wash both precipitates separately, and then digest them together, in an evaporating dish, with **ammonium sulphide.** Filter, and wash.† [For **Ce, Be, U, Ti,** and **Tl,** see 251.]

Precipitate : FeS, MnS, CoS, NiS, ZnS ; $Al_2(PO_4)_2$, $Cr_2(PO_4)_2$; $Al_2(OH)_6$, $Cr_2(OH)_6$; Ba, Sr, Ca, and **Mg Phosphates.**

Dissolve the precipitate in a test-tube by hot dilute **hydrochloric acid,** with addition of a minute fragment of **potassium chlorate.** Digest to expel free chlorine, and filter out any free sulphur. Nearly neutralize with a dilute solution of sodium or potassium carbonate and add solution of sodium or **Potassium Acetate strongly acidified with Acetic Acid,** as long as a precipitate results. Digest with gentle heat, and filter while hot.

Precipitate : $Fe_2(PO_4)_2$, $Al_2(PO_4)_2$, $Cr_2(PO_4)_2$.

Boil the precipitate, for some time, with **Potassium** or sodium **hydrate** (free from **Al**).

Residue : $Fe_2(PO_4)_2$, $Cr_2(PO_4)_2$.

(1.) For *Chromium,* oxidize a portion of the residue (or of the precipitate before treatment with alkali), according to directions in the Table at 242.

(2.) For *Iron,* dissolve a portion of the residue (or of the precipitate before boiling with alkali) and test by **potassium sulphocyanate.**

Solution : $K_2Al_2O_4$, with **K_3PO_4.**

Acidulate with **HCl,** and add excess of **ammonium hydrate.**

Precipitate : $Al_2(PO_4)_2$, not soluble in acetic acid.

To separate the aluminium from the **PO_4,** fuse with silica, as directed in 148.

Solution : $[Fe_2Cl_6, Al_2Cl_6, Cr_2Cl_6]$ or **H_3PO_4 ; $MnCl_2$, $CoCl_2$, $NiCl_2$, $ZnCl_2$; $BaCl_2$, $SrCl_2$, $CaCl_2$, $MgCl_2$.**

Add **Ferric Chloride,** drop by drop, as long as a precipitate results, and until the liquid turns red, and digest, for some time, at gentle heat. Filter out and reject the precipitate, **$Fe_2(PO_4)_2$.** Examine the filtrate for Third Group bases and alkaline earths, in absence of **PO_4.** This may be done as follows :

To the filtrate (or solution not precipitated by ferric chloride) add **ammonium chloride** and **ammonium hydrate,** and filter.

Precipitate : $Al_2(OH)_6$, $Cr_2(OH)_6$, $[Fe_2(OH)_6]$.

Test for *Aluminium* and *Chromium,* as directed for Group III. A, in the Table at 242.

For *Iron,* if not found in the precipitate by Acetate, test the original solution by 193.

To the filtrate add **Ammonium Sulphide,** and digest and filter.

Precipitate : MnS, CoS, NiS, ZnS.

Treat as directed for Group III. B, in the Table at 242.

Solution : May contain **Ba, Sr, Ca, Mg.**

Treat as directed in the Tables for Groups IV. and V. (798 and 799).

* Alkaline earth metals, found in this filtrate, are in excess of the quantity held as phosphates.

† Phosphoric acid found here, shows that **Fe, Mn, Co,** and other Third Group phosphates, had been formed, and then decomposed by the ammonium sulphide.

249. *Oxalates* have nearly the same deportment in the third group as phosphates, but the oxalic acid radical is decomposed altogether by the ignition and oxidation directed in 243 (*c*). By the same operation the fluorine of *fluorides* is expelled, and the silica of *silicates* left behind in the residue. *Boracic acid* is precipitated slightly in the third group of bases, but very little if ammonium chloride is added in large proportion.

250. The use of Barium Carbonate for separation of the pseudo-triads from the dyads of the third group has been described in 246, as used in the Table at 797. The following is another scheme with use of this reagent :

Plan for Separation by Barium Carbonate.

Dissolve the third group precipitate in hydrochloric acid with a little potassium chlorate (to oxidize ferrosum); digest with gentle heat to expel all the free chlorine; neutralize with potassium carbonate; filter, if necessary; add the *barium carbonate*, agitate, and leave to subside in a flask or test-tube corked close to exclude the air. Decant, filter; wash with hot water.

Precipitate (*a*) : $Fe_2(OH)_6$, $Cr_2(OH)_6$, etc. (the excess of $BaCO_3$).

Solution (*b*) : $ZnCl_2$, $MnCl_2$, $CoCl_2$, $NiCl_2$; ($BaCl_2$).

Dissolve precipitate (*a*) in dilute hydrochloric acid; add dilute sulphuric acid to complete the precipitate. Filter.

Precipitate : $BaSO_4$. (Reject.)

Solution (*c*) : Fe_2Cl_6, Cr_2Cl_6, Al_2Cl_6.

Nearly neutralize solution (*c*) with potassium carbonate; add *excess of potassium hydrate*, and boil for a few minutes. Filter.

Precipitate (*d*) : $Fe_2(OH)_6$, $Cr_2(OH)_6$.

Solution (*e*) : $K_2Al_2O_4$. (Determine by 145.)

Fuse precipitate (*d*) *with* sodium carbonate and *nitrate*. Dissolve in hot water, and filter.

Residue (*f*) : $Fe_2(OH)_6$. (Dissolve in hydrochloric acid ; test by 193.)

Solution (*g*) : K_2CrO_4. (Test by 163, etc.)

To solution (*b*), add sulphuric acid to complete the precipitate; filter out the barium sulphate; nearly neutralize the filtrate with potassium carbonate; *add excess of potassium hydrate;* boil a very short time, and filter.

Solution (*h*) : K_2ZnO_2. (Add hydrosulphuric acid, 237.)

Precipitate (*i*) : $Mn(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$.

Wash precipitate (*i*), dissolve in a little dilute hydrochloric acid, nearly neutralize with ammonium hydrate; add ammonium acetate, and *treat thoroughly with hydrosulphuric acid.* Filter.

Precipitate (*j*) : CoS, NiS.

Solution (*k*) : $Mn(C_2H_3O_2)_2$. (Add ammonium hydrate and sulphide—204, etc.)

Dissolve precipitate (*j*) in hydrochloric acid with a little potassium chlorate; nearly neutralize with potassium carbonate; add solution of *potassium cyanide*, sufficient barely to redissolve the precipitate at first produced. Boil thoroughly, cool, and filter; add strong solution of good *sodium hypochlorite*, leave for some time in a warm place (as long as a black precipitate continues to form), and filter (230).

Precipitate (*l*) : $Ni_2(OH)_6$.

Solution (*m*) : $K_3(CoCy_6)$. (Evaporate to dryness ; test by 217, etc.)

CERIUM, BERYLLIUM, URANIUM, TITANIUM, THALLIUM.

251. Cerium and Beryllium are **classed** with the metals of the *earths;* Uranium with the metals *allied to iron ;* Titanium resembles tin in some reactions and *silicon* in others, forms an acidulous anhydride as its most stable oxide, and appears in the third group in consequence of the precipitation of this acid from its acid solutions by alkalies. Thallium resembles lead in some particulars, and the alkali metals in others.

Cerium, Beryllium, Titanium, and Uranium, appear in Group III. A ; the first three not forming sulphides. Of the four, beryllium only is dissolved from the hydrate by excess of fixed alkali, none by ammonium hydrate. Thallium, as a monad, appears in the first group ; as a triad, in Group III. A, in the same way as ferricum.

252. CERIUM forms two *oxides*, Ce_2O_3 or cerous, and CeO_2 or ceric oxide ; also Ce_3O_5 or ceroso-ceric oxide is formed by exposure of cerous oxide to the air, and is the most stable oxide. The most stable *salts* of this metal are the cerous ; ceroso-ceric salts are formed, but mostly reduced to the cerous combination by boiling their solutions ; the existence of ceric salts is uncertain.—**Potassium** or sodium hydrate, precipitates from cerous salts the hydrate, $Ce(OH)_3$, white; changing by chlorine or other oxidizing agents to ceroso-ceric hydrate, yellow.—**Ammonium hydrate** precipitates a basic salt. Alkalies do not redissolve their precipitates.—Alkaline **carbonates** precipitate white cerous *carbonate*, $Ce_2(CO_3)_3$.—**Oxalates** precipitate cerous oxalate, white; first gelatinous, then crystalline, converted by ignition into ceroso-ceric oxide.—Potassium **Sulphate** precipitates potassio-cerous sulphate, $(K_2SO_4)_3Ce_2(SO_4)_3$, white, crystalline, insoluble in excess. —**Ferrocyanides** precipitate white cerous ferrocyanide.—Hydrosulphuric acid **separates** from cerium the metals of the second group; saturated solution of potassium sulphate separates cerium from zinc, chromium, manganese, iron, cobalt, nickel; also from the earth metals.—Barium Carbonate precipitates cerium very slowly. The reaction with oxalic acid is characteristic.—With borax and microcosmic salt, all compounds of cerium give, with the oxidizing **blow-pipe** flame, a bead, deep red while hot, colorless when cold; with the reducing flame, when strongly saturated, a yellow enamelled bead.

253. BERYLLIUM (glucinum) resembles aluminium. It forms a single oxide, BeO, and a single *class of salts*, but forms many basic salts.—**Fixed alkali hydrates** precipitate the *hydrate*, $Be(OH)_2$, resembling aluminium hydrate, soluble in excess; **ammonium hydrate** causes the same precipitate, insoluble in excess or in cold solution of ammonium salts.—Alkali *sulphides* also precipitate the hydrate.—**Carbonates** precipitate double carbonates, or basic carbonates of beryllium, soluble in ammonium carbonate. Barium carbonate precipitates the chloride, even in the cold.—**Phosphates** throw down $BeHPO_4$, flocculent. Oxalates cause no precipitate.—**Ferrocyanide** of potassium causes, after some time, a gelatinous precipitate.—Beryllium is separated and distinguished from aluminium, and from zinc, by the solubility of its hydrate and carbonate in excess of ammonium carbonate ; from zinc by the indifference of its alkaline solutions to ammonium sulphide. Dilute alkaline solutions precipitate on long boiling, also, the hydrate dissolves in ammonium chloride solution on boiling, both distinctions from aluminium.—Beryllium compounds, **ignited** with cobalt nitrate, yield a gray mass. Soluble salts of beryllium have a sweet **taste.**

254. URANIUM, comparable with iron, is heavier, less easily reduced, and more easily oxidized, chlorinized, or sulphidized, than that metal. Besides uranous and uranic *oxides*, UO_2 brown and UO_3 brick-red, there are two intermediate oxides, U_3O_8 green and U_2O_5 black. Uranium acts as a base in two *classes of salts*—having nearly the same stability as the corresponding salts of iron, *uranous* salts with a green color and *uranic* salts bright yellow; uranic oxide also acts as an acidulous anhydride, combining with bases to form stable uranates having a yellow color. The uranic oxy-salts are *basic*, as uranic nitrate, $UO_2(NO_3)_2$; uranic sulphate, $UO_2(SO_4)$; and the haloid uranic salts all contain oxygen; uranic oxy-chloride, UO_2Cl_2; oxy-bromide, UO_2Br_2.

Uranous oxide and hydrate dissolve in hydrochloric and sulphuric acids to uranous salts; in nitric acid to uranic salt. Uranic oxide and hydrate dissolve in acids to uranic salts.

a. **Uranous Salts** are precipitated by **alkalies** as red-brown uranous hydrate, $U(OH)_4$, insoluble in excess and in ammonium salts, soon oxidizing in the air to yellow uranic oxide and uranate of the alkali metal. Alkali **carbonates** precipitate (green) basic carbonate or hydrate, *soluble in excess* of the precipitant, especially of ammonium carbonate or fixed alkaline acid carbonates, to a green solution.—Alkaline **sulphides** precipitate the black uranous sulphide, US_2, soluble in very dilute acids, hence not formed from neutral salts by hydrosulphuric acid. **Phosphates** give a green uranous phosphate, quite soluble in acids when recent, not when dry; **oxalates** a gray-green, and **ferrocyanides** a light brown precipitate.

b. **Uranic salts** are precipitated by **alkalies** as yellow compounds of uranic oxide and alkali—as $K_2O.(UO_3)_2.(H_2O)_3$—*insoluble in excess of the reagent and in ammonium salts.* Alkali **carbonates** precipitate yellow double carbonates—as $K_4(UO_2)(CO_3)_3$—*soluble in excess* of the precipitant, especially of ammonium carbonate or fixed alkali hydrogen carbonate (separation from **Al, Fe,** etc.) From these solutions, potassium hydrate precipitates the uranic oxide; the solution in excess of carbonate of ammonium is precipitated by boiling. Barium carbonate precipitates uranic salts completely, a separation from third-group dyads. **Hydrosulphuric acid** reduces uranic to uranous salt with precipitation of sulphur only; **sulphide** of ammonium precipitates uranous sulphide, US_2, black; **phosphates** throw down uranic phosphate, yellowish-white, $(UO_2)H(PO_4)$, insoluble in acetic acid; **oxalates,** a gray-green uranic oxalate $(UO_2)C_2O_4$; crystalline, soluble in hot, and nearly insoluble in cold water; **ferrocyanides,** a deep red-brown precipitate—a delicate test; ferricyanides, no change.

c. **Ignition** on charcoal does not reduce oxides of uranium to the metallic state. Borax and microcosmic salt give, with compounds of uranium, in the outer flame, clear yellow **beads** greenish-yellow when cold; in the inner flame, green beads, deeper when cold.

255. TITANIUM is a metal bearing somewhat singular relations. It forms very stable compounds with nitrogen and cyanogen (furnace products); it decomposes water at the boiling temperature, and burns brilliantly in the air. In its most stable compounds it acts as a tetrad; titanic oxide, TiO_2, acting as *an acidulous anhydride* toward bases and having properties and salts resembling those of silicic acid—likewise forming a full series of (quadrivalent) *titanic salts*, as $TiCl_4$. The metal also acts as a pseudo-triad, in *titanous* oxide, Ti_2O_3, titanous chloride Ti_2Cl_6, and a few other salts, all powerful reducing agents.

a. **Titanous salts** make violet-colored solutions (the chloride, nitrate, and sulphate dissolve in water), from which **alkali hydrates** and their **carbonates** precipitate titanous hydrate, $Ti_2O_3(H_2O)x$, dark brown, changing in the air to titanic acid, H_2TiO_3; ammonium **sulphide** throws down the same precipitate, hydrosulphuric acid producing no change; calcium carbonate separates the hydrate.—Ferric and cupric salts are reduced to

ferrous and cuprous compounds, and from salts of mercury, silver and gold, the metals are separated, by titanous salts, which are thereby changed to titanic compounds.

b. **Titanic salts** are mostly insoluble in **water,** or decomposed by it with precipitation of titanic acid, $H_2O.TiO_2$ or H_2TiO_3. Of this compound, there are *two modifications,* one soluble and one insoluble in hydrochloric and nitric acids; strong sulphuric acid dissolves both modifications; but the titanic sulphate is decomposed and precipitated on dilution, and the chloride on long boiling (distinctive). Titanic chloride, $TiCl_4$, and nitrate, $Ti(NO_3)_4$, are permanently soluble in water.—From these, **Alkalies** and their **carbonates** and **sulphides** throw down the white voluminous *titanic hydrate* or titanic acid, insoluble in excess of the precipitants, and in ammonium salts; the same precipitate is produced by **barium carbonate. Ferrocyanide** of potassium gives a dark-brown precipitate of titanic ferrocyanide; **tannic acid,** an orange precipitate.

c. **Titanates,** as shown above, are not formed by treating titanic acid, even when recent, with aqueous alkalies, but are produced by fusion of titanic acid with alkalies or their carbonates. So prepared, the neutral alkali titanates have a yellow color, and are decomposed by hot water with separation of insoluble acid titanates of the same bases, but soluble in acids as titanic salts.

d. Compounds of titanium acids with **microcosmic salt,** dissolve in the outer flame to a clear **bead,** pale yellow when hot, and colorless when cold. The strong reducing flame now turns the bead yellow while hot (reddish when cooling), and *violet* when cold (titanous oxide). If sulphate of iron be added, the bead by the inner flame is blood-red. In the borax bead the same reactions are obtained, less intense.—**Ignition** on charcoal with soda does not reduce titanium to the metallic state (distinction from tin).

256. **THALLIUM** is a metal of exceptional character; in density, fusibility, atomic weight, and insolubility of its lower chloride and of both its iodides, it resembles lead, and is allied to Group I.; in the solubility of its hydrates and carbonate, it ranks with the metals of the alkalies.* It oxidizes readily in the air, vaporizes and burns at the red heat, but does not decompose cold or boiling water. It is precipitated from salts by zinc, in spongy form. As a monad, its compounds are stable, and not easily oxidized; as a triad, it is easily reduced to the univalent condition.

a. **Thallious** oxide, Tl_2O, is black; on contact with water, it forms a hydrate, $TlOH$, freely soluble in water and in alcohol, to colorless solutions. The carbonate is soluble in about 20 parts of water; the sulphate and phosphate are soluble; the chloride very sparingly soluble; the iodide insoluble in water. **Hydrochloric acid** precipitates from solutions not very dilute, *thallious chloride,* $TlCl$, white, and unalterable in the air. As a first group precipitate, thallious chloride dissolves enough in hot water to give the light yellow precipitate of *iodide,* TlI, on adding a drop of **potassium iodide** solution—the precipitate being slightly soluble in excess of the reagent. **Hydrosulphuric acid** precipitates the acetate, and slightly precipitates strongly acidified solutions, as Tl_2S, black, having the solubilities of zinc sulphide, and in the air soon oxidized to sulphate. **Ammonium sulphide** causes a complete precipitation. **Ferrocyanides** give a yellow precipitate, Tl_4FeCy_6; **phosphomolybdic acid** a yellow precipitate; and potassium **permanganate,** a red-brown precipitate, consisting in part of Tl_2O_3. **Chromates** precipitate yellow, normal chromate; and **platinic chloride,** pale orange, *thallious platinic chloride,* $(TlCl)_2PtCl_4$. Thallium compounds readily impart an intense green color to the **flame,** and one emerald green line to the **spectrum** (the most delicate test). The flame-

* Occurring in minute quantities in certain iron and copper pyrites, thallium sometimes contaminates crude sulphur, and commercial sulphuric and hydrochloric acids.

color and spectrum, from small quantities, are somewhat evanescent, owing to rapid vaporization.

b. **Thallic** oxide, Tl_2O_3, dark violet, is insoluble in water; the hydrate, an oxy-hydrate, TlO(OH), is brown and gelatinous. This hydrate is precipitated from thallic salts by the caustic **alkalies**, and not dissolved by excess. **Chlorides** and **bromides** do not precipitate thallic solutions; **iodides** precipitate **TlI** with **I**. **Sulphides**, and H_2S, precipitate *thallious sulphide*, with sulphur. Thallic oxide, suspended in solution of potassium hydrate, and treated with **chlorine**, develops an intense violet red color. Thallic chloride and sulphate are reduced to thallious salts, by boiling their water solutions.

257. The leading reactions of the remaining rare metals of the Third Group, are given in the following Comparative Table. The six metals first named form *earthy* oxides; tantalum and niobium, like titanium, form acids. Indium and vanadium, also forming acids, can be placed in the Second Group.

	Zr	Th	Y	E	La	D	Ta	Nb	In	V
NH_4OH with NH_4Cl.	$Zr(OH)_4$	$ThO(OH)_2$	$Y(OH)_3$ §	$E(OH)_3$	$La(OH)_3$	$Di(OH)_3$ *	$HTaO_3$ **	. . . .	$In(OH)_3$	¶¶
$(NH_4)_2S$	$Zr(OH)_4$	$ThO(OH)_2$	$Y(OH)_3$	$E(OH)_3$	$La(OH)_3$	Pre. *	$HTaO_3$	$HNbO_3$	In_2S_3 §§	‖‖
KOH or NaOH, excess.	Pre.	Pre.	Pre.	Pre.	Pre. ¶	Pre.	† †	‡‡	Pre.	
K_2CO_3, excess.	Sol. * †	Sol. †	Pre. *	Pre. *	Pre.	Pre.	. . . .	. . . .	Pre.	
$(NH_4)_2CO_3$, excess.	Sol. †	Sol. †	Sol. *	Sol. *	Pre.	Pre.	. . . .	. . . .	Sol. *	
$BaCO_3$, cold.	No pre.	Pre.	No pre.	No pre.	Pre.	Pre. *	. . . .	. . . .	Pre.	
K_2SO_4	Pre.	Pre. ‡	No pre.	No pre. ‖	Pre. *	Pre.	. . . .	. . . .	. . . .	
$H_2C_2O_4$	Pre.	Pre.	Pre.	Pink pre.	Pre.	Pre.	. . . .	No pre.	Pre. *	
K_4FeCy_6	. . . .	Wt. pre.	Wt. pre.	. . . .	. . . .	Wt. pre.	. . . .	Red pre.	Wt. pre.	Yel. pre.
K_3FeCy_6	. . . .	No pre.	No pre.	. . . .	. . . .	. . . .	. . . .	Yel. pre.	. . . .	
$Na_2S_2O_3$	Pre.	Pre. *	No pre.	. . . .	. . . .	No pre.	. . . .	. . . .	Pre. *	

* In part. † Reprecipitated on boiling. ‡ In boiling, concentrated solutions, slowly but completely.

§ Slightly soluble in ammonium chloride. ‖ Partial pre. in the cold, dissolving when warm.

¶ When the acetate is precipitated by excess of ammonia, and the washed precipitate treated with iodine, a blue color appears. ** Or $NH_4H(TaO_3)_2$.

†† Fusion with KOH gives $KTaO_3$, soluble in water; with NaOH, $NaTaO_3$, insoluble in solution of sodium hydrate. The sol. of $KTaO_3$ is pre. by CO_2; also by HCl (as Ta_2O_3) soluble in excess.

‡‡ Solutions of niobates, as $KNbO_3$, are pre. by mineral acids, as $HNbO_3$. In acidulated solutions, zinc forms a blue color (characteristic), lower oxide being formed.

§§ Formed yellow, in slightly acid solutions, by H_2S, soluble in excess of $(NH_4)_2S$, and in HCl.

‖‖ In neutral solutions, a brown color; on acidulating, a brown pre., Va_2S_5. H_2S reduces vanadates to Va_2O_4, with blue color. Acid solutions of Va_2O_3, are green; of Va_2O_5, red.

¶¶ For the characteristics of the several conditions of this element, see Watts's Dictionary, Vols. V. and VI.

GROUP II.

258. Metals whose Sulphides are Insoluble in Dilute Acids.

Copper,	Cu	= 63.0	Cu'' In cupric compounds. Cu_2'' In cuprous compounds.
Bismuth,	Bi	= 210.0	Bi''' In bismuthous compounds.
Cadmium,	Cd	= 111.6	Cd''
Lead,	Pb	= 206.4	Pb''
Silver,	Ag	= 107.66	Ag'
Mercury	Hg	= 199.8	Hg'' In mercuric compounds. Hg_2'' In mercurous compounds.
Arsenic,	As	= 74.9	As''' In arsenious compounds. As^{V} In arsenic compounds.
Antimony,	Sb	= 122.0	Sb''' In antimonious compounds. Sb^{V} In antimonic compounds.
Tin,	Sn	= 117.8	Sn'' In stannous compounds. Sn'''' In stannic compounds.
Gold,	Au	= 196.2	Au''' In auric compounds.
Platinum,	Pt	= 196.7	Pt'''' In platinic compounds.
Palladium,	Pd	= 106.2	Pd'' In palladious compounds.
Ruthenium,	Ru	= 103.5	Ru_2^{VI} In ruthenic compounds. RuO_3, ruthenic anhydride.
Iridium,	Ir	= 196.7	Ir_2^{VI}, In iridic oxide. Ir'''' In iridic dioxide.
Rhodium,	Rh	= 104.1	Rh_2^{VI} In rhodic salts.
Osmium,	Os	= 198.6	Os_2^{VI} In osmic double salts.
Tellurium,	Te	= 128.0	Te'' In tellurides. Te'''' In tellurites (dibasic). Te^{VI} In tellurates (dibasic).
Selenium,	Se	= 78.0	Se'' In selenides. Se'''' In selenites. Se^{VI} In selenates (dibasic).
Tungsten,	W	= 184.0	W^{VI} In tungstates (dibasic).
Molybdenum,	Mo	= 96.0	Mo'''' In molybdic compounds. Mo^{VI} In molybdates (dibasic).

259. The metals included in this group are **less strongly electro-positive** than those of the other groups. Only bismuth, antimony, tin, and molybdenum decompose water, and these only slowly and at high temperatures. The oxides of silver, mercury, gold, platinum, and palladium, are decomposed below a red heat. Copper, lead, and tin, tarnish by oxidation in the air. In general, the second group metals either do not dissolve in acids with evolution of hydrogen, or do so with difficulty. Nitric acid is the best solvent for all, except antimony and tin, which are rapidly oxidized by it.

260. Mercury, arsenic, antimony, and tin, form, each, two stable classes of salts. Therefore, the lower oxides, chlorides, etc., of these metals act as reducing agents; and their higher oxides, chlorides, etc., as oxidizing agents, each to the extent of its chemical force. Arsenic, antimony, tin, molybdenum, and several of the rare metals of this group, enter into *acidulous* radicals, which form stable salts. Arsenic and selenium are metalloids rather than metals. Arsenic, antimony, and bismuth, belong to the Nitrogen Series of Elements, the gradations of which are given in 584.

261. A large proportion of the compounds of the second group metals are **insoluble** in water. Of the oxides or hydrates, only the acids of arsenic are soluble in water. The only insoluble chlorides, bromides, and iodides, are in this group. The sulphides, carbonates, oxalates, phosphates, borates, and cyanogen compounds, are insoluble. Most of the so-called soluble compounds of bismuth, antimony, and tin, and some of those of arsenic and mercury, dissolve only in acidulated water, being decomposed by pure water, with formation of insoluble basic salts.

262. The oxides of arsenic, antimony, and tin—in general terms—**dissolve in alkali hydrates.** Oxides of silver, copper, and cadmium dissolve in ammonium hydrate; oxide of lead, in fixed alkali hydrate. Metallic lead, like zinc, dissolves in fixed alkali hydrate, with evolution of hydrogen, though it scarcely decomposes any acid by displacing hydrogen.

263. Many **double salts** are formed with the metals of this group. Those whose sulphides dissolve in alkali sulphides, owe this property to the formation of soluble sulpho-salts or double sulphides. Platinum forms a large number of stable double chlorides, soluble and insoluble; and gold forms double chlorides, cyanides, etc.

264. Mercury, antimony, silver, and gold, do not form **hydrates.** The oxides of gold are very instable.

265. The metals of this group are all easily reduced to the metallic state by **ignition on charcoal.** Except mercury and arsenic, which *vaporize*, and certain rarer metals difficultly fusible, the reduced metals melt to metallic grains on the charcoal. Mercury and antimony vaporize from the liquid, arsenic from the solid state.

COPPER.

266. Copper does not **dissolve** in acids with evolution of hydrogen; it dissolves most readily in nitric acid, chiefly with the evolution of nitric oxide (*a*); also, in hot concentrated sulphuric acid, with evolution of sulphurous anhydride (*b*):

$$a.\ 3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$$

$$b.\ Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$$

267. The atmosphere oxidizes copper very rapidly when in contact with solvents of the oxide of copper; and in this manner the metal becomes **oxidized and dissolved** in hydrochloric acid and nearly all acids, in ammonium hydrate, in solutions of many salts, in fats, sugars, and other organic substances.

268. Copper forms **two oxides,** and corresponding series of salts: *cuprous salts* being infrequent and instable compounds, nearly all insoluble in water, and easily resolved into metallic copper and *cupric salts*, the stable and representative compounds of the metal.

269. Cupric salts are readily **reduced to cuprous** combinations by most strong reducing agents acting *with alkalies*, as, by sulphites (*a*) with free alkali (difficultly, without alkali); by arsenious acid, with excess of alkali; by glucose, and certain other sugars and organic materials, with excess of alkali. Also, by ferrous salts, in presence of iodides (279 *b*). Metallic iron and zinc separate, from solutions of cupric salts, metallic copper, without formation of cuprous salt.

$$a.\ 2CuSO_4 + 4KOH + SO_2 = Cu_2SO_4 + 2K_2SO_4 + 2H_2O$$

270. CUPROUS oxide—Cu_2O—is of a brownish red **color**; cuprous hydrate—$Cu_2(OH)_2$—brownish yellow. Cuprous salts are **insoluble** in water. The chloride, Cu_2Cl_2, dissolves in strong hydrochloric acid to a colorless solution, which turns green in the air.

From this solution, water throws down the cuprous chloride, white; **fixed alkalies,** in small quantity, neutralize the free acid, and precipitate the white cuprous chloride; in larger quantity, precipitate the yellow cuprous hydrate, insoluble in excess. **Ammonium hydrate** and ammonium carbonate, in excess, redissolve the hydrate, and dissolve the oxide to a colorless solution, which turns blue on exposure (274). Potassa reprecipitates the ammonia solution. Soluble **carbonates** precipitate the yellow cuprous carbonate, Cu_2CO_3.—**Iodide** of potassium precipitates the white cuprous iodide, Cu_2I_2, without liberation of iodine (279, *b*).—Hydrosulphuric acid and **sulphides** precipitate Cu_2S, black.—**Phosphates, oxalates, cyanides,** and **ferrocyanides,** precipitate their respective cuprous salts, white; **ferricyanides,** brown-red.—With the **blow-pipe,** cuprous salts behave like cupric compounds (282).

271. CUPRIC oxide is black; the hydrate, light blue. Cupric salts, in crystals or solution, have a green or blue **color**; the chloride (2 *aq.*) in solution is emerald-green when concentrated, light blue when dilute; the sulphate (5 *aq.*) is "blue vitriol." Anhydrous cupric salts are white. The crystallized chloride is **deliquescent**; the sulphate, permanent; the acetate, efflorescent.

272. Cupric hydrate, basic carbonate, oxalate, phosphate, borate, arsenite, sulphide, cyanide, ferrocyanide, ferricyanide, and tartrate, are **insoluble** in water. The ammonio-oxide and most of the ammonio salts, the potassio and sodio cyanides, and the potassio and sodio tartrate, are soluble in water. In alcohol, the sulphate and acetate are insoluble; the chloride and nitrate, soluble. Ether dissolves the chloride.

Copper is easily **identified** by reduction with iron to the lustrous metallic state (280); also, by the blue solution with excess of ammonium hydrate (274), used as a separation from bismuth.

273. Fixed alkalies—KOH—added *to saturation* in solutions of copper salts—precipitate copper *hydrate*, $Cu(OH)_2$, deep blue, insoluble in excess, soluble in ammonium hydrate (if too much fixed alkali is not present), very soluble in acids and changed by boiling or by standing, to the black, basic hydrate, $Cu_3O_2(OH)_2$. If tartaric acid, citric acid, grape sugar, milk sugar, or certain other **organic** substances are present, the precipitate either does not form at all, or redissolves in excess of the fixed alkali to a blue solution. The tartrate alkaline solution may be boiled without change; in presence of sugar, the application of heat precipitates the yellow cuprous hydrate (280). The addition of alkali hydrates, *short of saturation*, forms insoluble basic salts, of a lighter blue than the hydrate.

274. Ammonium hydrate, added short of saturation, precipitates the pale blue basic salts; added just to saturation, the deep blue hydrate (in both cases *like the fixed* alkalies); added to supersaturation, the precipitate dissolves to an intensely deep blue solution. The blue solution consists of compounds of cuprammonium, $(N_2H_6Cu)''$, a diammonium formed by the substitution of an atom of copper for an atom of hydrogen in each of two semi-molecules of ammonium, NH_3NH_3Cu. The cuprammonium oxide is united with ammonium salt, as $(N_2H_6Cu)O.(NH_4)_2SO_4$ and $(N_2H_6Cu)O.(NH_4Cl)_2$:

$$CuSO_4 + 4NH_4OH = (N_2H_6Cu)O.(NH_4)_2SO_4 + 3H_2O$$

From this solution the fixed alkalies in strong solution precipitate the blue hydrate, and on boiling the black oxide, CuO.

275. Ammonium carbonate, like ammonium hydrate, precipitates and redissolves to a blue solution. **Carbonates** of fixed alkali metals—as K_2CO_3—precipitate the greenish-blue, basic *carbonate*, $Cu(OH)_2CuCO_3$, of variable composition, according to conditions, and converted by boiling to the black, basic hydrate (273), and finally to the black oxide. Barium carbonate precipitates only on boiling, a basic carbonate.

276. Hydrosulphuric acid, and soluble **sulphides,** precipitate *copper sulphide,* **CuS,** black, formed alike in acid solutions (distinction from iron, manganese, cobalt, nickel), and in alkaline solutions (distinction from arsenic, antimony, tin).—Solutions containing only the one-hundred-thousandth of copper salt are colored brownish by the reagent. The precipitate, **CuS,** is easily soluble by nitric acid (*a*) (distinction from mercuric sulphide); with difficulty soluble by strong hydrochloric acid (distinction from antimony); insoluble in hot dilute sulphuric acid (distinction from cadmium); insoluble in fixed alkali sulphides, and but slightly soluble in ammonium sulphide (distinction from arsenic, antimony, tin); soluble in solution of potassium cyanide (*b*) (distinction from lead, bismuth, cadmium. mercury); soluble in solution of potassium carbonate.

a. $3CuS + 8HNO_3 = 3Cu(NO_3)_2 + 3S + 4H_2O + 2NO$

b. $CuS + 4KCy = (KCy)_2CuCy_2 + K_2S$

277. Phosphates—as Na_2HPO_4—give a bluish-white precipitate of *copper phosphates;* $CuHPO_4$, if the reagent is in excess; $Cu_3(PO_4)_2$, if the copper salt is in excess; the precipitates slightly soluble by acetic acid.—**Oxalates** precipitate *cupric oxalate,* CuC_2O_4, bluish-white, insoluble in acetic acid, and formed from mineral acid salts of copper by oxalic acid added with alkali acetates.—Normal potassium **chromate** precipitates brown-red basic cupric chromate, somewhat soluble in water.—**Arsenites,** as K_3AsO_3, or arsenious acid with just sufficient alkali hydrate to neutralize it, precipitate from solutions of cupric salts (not the acetate), the green *copper arsenite,* chiefly $CuHAsO_3$ (Scheele's green, "Paris green"), readily soluble in acids and in ammonium hydrate, decomposed by strong potassium hydrate solution. From cupric **acetate,** arsenites precipitate, on boiling, *copper aceto-arsenite,* $(CuO\text{-}As_2O_3)_3Cu(C_2H_3O_2)_2$, Schweinfurt green, or Imperial green, "Paris green," dissolved by ammonium hydrate and by acids, decomposed by fixed alkalies.

278. Alkaline **cyanides**—as **KCy**—precipitate at first the yellowish-green *cyanide,* $CuCy_2$, soluble in excess of the reagent by formation of potassium cupric cyanide, $(KCy)_2CuCy_2$. The cupric cyanide precipitate is instable, becoming cuprous, or cuproso-cupric cyanide, Cu_2Cy_2; the latter unites with ammonium hydrate, forming several green to blue salts, mostly soluble in water. **Ferrocyanides**—as K_4FeCy_6—precipitate the *copper ferrocyanide,* Cu_2FeCy_6, reddish-brown, insoluble by acids, decomposed by alkalies. In highly dilute solutions, a reddish coloration, without precipitate, is seen. **Ferricyanides**—as K_3FeCy_6—precipitate *copper ferricyanide,* $Cu_3(FeCy_6)_2$, yellowish-green, insoluble in hydrochloric acid. **Sulphocyanates,** with sulphurous acid, precipitate *cuprous sulphocyanate,* $Cu_2(CyS)_2$, white (distinction from cadmium).

279. Soluble **iodides** precipitate, from concentrated solutions of *copper*

salts, *cuprous iodide*, Cu_2I_2, white, colored dark brown by the *iodine* separated in the reaction (*a*). The iodine dissolves with color in excess of the reagent, or dissolves colorless on adding ferrous sulphate or soluble sulphites, by entering into combination. Cuprous iodide dissolves in thiosulphates (with combination).

The cuprous iodide is precipitated, free from iodine, and more completely, by adding *reducing agents* with iodides; as, Na_2SO_3, H_2SO_3, $FeSO_4$ (*b*).

a. $2CuSO_4 + 4KI = Cu_2I_2 + 2I + 2K_2SO_4$

b. $2CuSO_4 + 2KI + 2FeSO_4 = Cu_2I_2 + K_2SO_4 + Fe_2(SO_4)_3$

$2CuSO_4 + 4KI + H_2SO_3 + H_2O = Cu_2I_2 + 2K_2SO_4 + H_2SO_4 + 2HI$

280. *Metallic copper* is reduced and separated from cupric solutions by **iron, zinc,** cobalt, nickel, lead, cadmium, bismuth, tin, and phosphorus. A bright slip of iron in solution of cupric salts acidulated with hydrochloric acid, receives a bright copper coating, recognizable from solutions in 120,000 parts of water. Zinc acts most promptly in contact with platinum, as by use of a platinum dish, when the copper is deposited on the platinum; when minutely divided as a precipitate, the copper is dark brown to black. Finely divided zinc can be removed by solution in hydrochloric acid. Nitric acid, and tartaric acid, interfere with this reaction:

$$CuSO_4 + Fe = Cu + FeSO_4$$

(For every 63 parts of copper deposited, 55.9 parts of iron are dissolved.)

For detection of minute **traces** of copper, by metallic reduction, Hager directs as follows: The material is obtained in solution acidulated with acetic acid. The end of a platinum wire is inserted just within the eye of a large sewing-needle, around which the wire is wound. The coil is left in the solution three or four hours, at a temperature of 25° to 30° C. (77° to 86° F.) The presence of copper is indicated by a black-brown coating on the platinum wire, but more closely determined by further treatment. The needle is now withdrawn, the platinum wire is washed by gentle introduction into water, placed in a test-tube, treated with four or five drops of nitric acid and a few drops of diluted sulphuric acid, warmed, boiled to expel all nitric acid, and an excess of ammonium hydrate added.

Arsenious acid (385 *d*), certain sugars, and many organic compounds, reduce cupric salts with fixed alkali hydrate, to a yellow precipitate of *cuprous oxide* and not to metallic copper.

Sodium thiosulphate, added to hot solutions of copper salts, gives a black precipitate of *cuprous sulphide*, with formation of sulphate and free sulphur. In solutions strongly acidulated (with hydrochloric acid), this is a separation from cadmium.

281. **Ignition** with sodium carbonate on charcoal leaves metallic copper in finely divided grains. The particles are gathered by triturating the charcoal

mass in a small mortar, with the repeated addition and decantation of water until the copper subsides clean. It is recognized by its color, and its softness under the knife.

282. Copper readily dissolves, from its compounds in **beads** of borax and of microcosmic salt, in the outer flame of the blow-pipe. The beads are green while hot, and *blue* when cold. In the inner flame, the borax bead becomes colorless when hot; the microcosmic salt turns dark green when hot, both having a reddish-brown tint when cold (Cu_2O), (helped by adding tin, 789).

283. Compounds of copper, heated in the inner flame, **color the outer flame** green. Addition of hydrochloric acid increases the delicacy of the reaction, giving a greenish-blue color to the flame.

BISMUTH.

284. A hard, brittle **metal**, of a moderate lustre and a reddish gray-white color, often iridescent from superficial oxidation, a crystalline laminated fracture, fusible at 264° C. (507° F.), and slightly volatile at high temperatures.

285. Bismuth is but slightly **oxidized** in the air at ordinary temperatures, rapidly at a red heat; it takes fire in chlorine, and unites readily with bromine, iodine, and sulphur. Hydrochloric acid scarcely attacks it; boiling sulphuric acid salifies it with separation of sulphurous anhydride, but it **dissolves** much the most readily in nitric acid, with evolution of lower oxides of nitrogen.

286. Bismuth forms one stable oxide, which is represented in permanent **salts**, *bismuthous oxide*, Bi_2O_3, yellow-white. Bismuth monoxide, **BiO**, black, is more readily oxidizable than the metal. Bismuthic anhydride, Bi_2O_5, brown, forms red bismuthates with the alkali metals, decomposed by water. Bismuthic acid, $HBiO_3$, is a red powder, insoluble in water. There are several intermediate oxides, unions of those here named. Bismuth is at the metallic extreme of the "nitrogen group," compared in 584. Bismuthous salts are not very easily affected by oxidizing or reducing agents; the hydrate, however, is reducible (297). They have an unusual tendency to *basic* formations—the chloride forming oxy-chlorides, etc. The chloride is **deliquescent**; the nitrate, permanent.

287. The sulphide, hydrate, basic carbonate, phosphate, chromate, borate, sulphite, oxalate, iodide (295), cyanide, ferrocyanide, ferricyanide, tartrate, citrate, tannate, and valerianate, are **insoluble** in water. The chloride, bromide (295), nitrate, chlorate, and sulphate—when taken as normal salts—are soluble in water acidulated with their respective acids, or with other acids forming "soluble" bismuth salts; but are decomposed by pure water, with partial solution and partial separation of insoluble *basic* salts—(261 and equations in 288). The ammonio citrate is soluble in water without decomposition; and the decomposition of the normal chloride, nitrate, and sulphate, is prevented by the addition of comparatively small quantities of acetic, citric, and certain other organic acids. The acidulated, water-saturated solutions of the nitrate and chloride may be considerably further diluted with alcohol, without disturbance.

In **analysis**, bismuth is precipitated alone, from the nitric acid solution of second group sulphides (455), after removing lead (and silver), by adding

excess of ammonium hydrate, a separation from copper and cadmium. The precipitation by water (288) suggests bismuth.

288. Water precipitates, from the acidulated bismuth solutions, white *basic salts* (see equations below), which contain less of their acid radicals in proportion as greater quantities of water are added, and some of which can be washed on the filter until almost pure hydrate or oxide. The precipitation is most complete with the chloride, and with other salts is promoted by addition of hydrochloric acid or **chlorides**; hence, it may occur as a first group precipitate. All the precipitates are readily soluble in hydrochloric and nitric acids; not in tartaric acid (distinction from antimony). Acidulation with certain organic acids (in accordance with the statement in 287) prevents the precipitation:

$$BiCl_3 + H_2O = BiOCl + 2HCl$$

$$Bi(NO_3)_3 + 2H_2O = (a)\ BiONO_3.H_2O + 2HNO_3$$

$$4Bi(NO_3)_3 + 6H_2O = (b)\ Bi_4O_5(NO_3)_2.H_2O + 10HNO_3$$

$$Bi(NO_3)_3 + 3H_2O = (c)\ Bi(OH)_3 + 3HNO_3$$

(*a*) $BiO(NO_3)$ or $Bi_2O_3.N_2O_5$

(*b*) $Bi_4O_5(NO_3)_2$ or $2Bi_2O_3.N_2O_5$

289. The **alkali hydrates** precipitate from bismuth solutions—in absence of tartaric acid, citric acid, and certain other organic substances—the white *bismuth hydrate*, $Bi(OH)_3$, insoluble in excess of the reagents, converted by boiling to the oxide, Bi_2O_3, yellowish-white. Certain reducing agents turn the precipitate black (297).

290. The **carbonates** precipitate *basic bismuth carbonate*, $Bi_2O_2CO_3$, white, insoluble in excess. Barium carbonate forms the same precipitate, without heating.

291. Hydrosulphuric acid and **sulphides** precipitate *bismuth sulphide*, Bi_2S_3, black, insoluble in dilute acids and in alkali hydrates; insoluble in alkali sulphides (distinction from arsenic, tin, antimony), and in alkali cyanides (distinction from copper). It is soluble by moderately concentrated nitric acid (distinction from mercury), the sulphur mostly remaining free.

292. Soluble **chromates**—both K_2CrO_4 and $K_2Cr_2O_7$—precipitate the yellow, basic *bismuth chromate*, $Bi_2O(CrO_4)_2$, distinguished from that of lead by its insolubility in fixed alkali hydrate.

293. Phosphoric acid and soluble **phosphates** precipitate *bismuth phosphate*, $BiPO_4$, insoluble in five per cent. nitric acid (distinction from other phosphates, except stannic phosphate), insoluble in dilute acetic acid, readily soluble in hydrochloric and sulphuric acids.—Arsenic acid and **arseniates** form a precipitate corresponding to the phosphate in composition, and having

the same solubilities. It will be seen, that free phosphoric and arsenic acids can precipitate nitrate, but not chloride of bismuth (19); phosphates and arseniates precipitate both.

294. Oxalic acid and **oxalates** precipitate *bismuth oxalate*, $Bi_2(C_2O_4)_3$, white, insoluble in dilute acids.

295. Potassium Iodide produces in slightly acidulated solutions of bismuth salts—not acidulated to excess with hydrochloric acid—a dark brown precipitate of *bismuth iodide*, partly basic, soluble in excess of the reagent, in hydrochloric acid and in hydriodic acid—in each case with a brown tinge to the solution, not soluble in dilute nitric acid.*

Bromides precipitate a basic salt, soluble in acid.

296. Alkaline **cyanides** precipitate the white *hydrate*, $Bi(OH)_3$, with formation of hydrocyanic acid. The precipitate is insoluble in the reagent.—**Ferrocyanides** form a white to yellow precipitate; **ferricyanides** a yellow to brownish-yellow precipitate—both normal bismuth salts, and both insoluble in acids.

Tannic acid throws down bismuth tannate, yellow.

297. *Metallic bismuth* is **reduced** from bismuthous solutions, mostly as a spongy precipitate, by **zinc, iron,** tin, lead, copper, and cadmium.

Potassium or sodium stannite (K_2SnO_2), when added in excess to bismuth solutions, causes a black precipitate, from reduction to *bismuth monoxide*, **BiO**, a very delicate reaction. The stannite is made, when wanted, by adding, to stannous chloride solution, in a test-tube, enough sodium or potassium hydrate to redissolve the precipitate at first formed (430).

The basic bismuth nitrate is reduced by **grape sugar,** in a warm solution of fixed alkali carbonate, with formation of a blackish-brown liquid and dark-gray sediment containing *bismuth monoxide.* Also, the recent bismuth hydrate, in suspension with the excess of fixed alkali, is reduced by digestion with grape sugar or milk sugar to a black precipitate.

298. On charcoal, with sodium carbonate, before the **blow-pipe,** bismuth is readily reduced from all its compounds. The *globule* is easily fusible, brittle (distinction from lead), and gradually oxidizible under the flame, forming an *incrustation* (Bi_2O_3), orange-yellow while hot, lemon-yellow when cold, the edges bluish-white when cold. The incrustation disappears, or is driven by the reducing flame, without giving color to the outer flame.

* This precipitate, at the moment of its formation in concentrated solutions, is doubtless normal bismuthous iodide, BiI_3, which is gradually decomposed by water, more rapidly in dilute solutions, forming basic iodide (oxy-iodide) with separation of hydriodic acid. The oxy-iodide of the composition **BiOI** is stated to be insoluble in solutions of alkali iodides, while this precipitate is soluble in these solutions, even after decomposition by much water.

The reaction of iodides, with bismuth solutions, differs in degree but not in kind from that of chlorides (288); the normal bismuth iodide only requiring stronger acidulation to hold it in solution than the normal chloride. Also, intermediate between the behavior of these two lies that of bismuthous bromide. The aqueous iodides form a very delicate test for even quite strongly acidulated solutions of bismuth salts, and the bismuthous iodide may not improperly be classed as an "insoluble" salt (287).

299. With borax or microcosmic salt, bismuth gives **beads**, faintly yellowish when hot, colorless when cold.

CADMIUM.

300. A tin-white, lustrous **metal**, softer, more fusible and more volatile than tin, melting at about 350° C. (662° F.), and vaporizing at 860° C. (1,580° F.) It oxidizes but slowly in the air at ordinary temperatures; at its boiling point it burns rapidly to oxide, which is not decomposed by heat alone. It **dissolves** slowly in hot, moderately dilute hydrochloric or sulphuric acid, with evolution of hydrogen; in nitric acid, more readily with generation of nitrogen oxides.—Cadmium forms a single oxide, **Cd″O**, yellowish-brown, and a corresponding series of salts, from which it is reducible, in the wet way, only by strong reducing agents. It forms numerous double salts, especially haloids.—The hydrate, sulphide, carbonate, oxalate, phosphate, cyanide, ferrocyanide and ferricyanide are **insoluble** in water. The chloride and bromide are **deliquescent**, and soluble in alcohol as well as water ; the iodide is permanent, and soluble in water and alcohol; very sparingly in ether. The ammonio-oxide and the potassio and sodio cyanides are soluble in water.

In **analysis**, cadmium is separated from other members of the second group, along with copper: and separated from copper, as sulphide (470).

301. Fixed **alkalies** precipitate from solutions of cadmium salts—in absence of tartaric and citric acids, and certain other organic substances—the white *hydrate*, $Cd(OH)_2$, insoluble in excess of the reagents (distinction from zinc). Ammonium hydrate forms the same precipitate, which it redissolves. Alkali **carbonates** precipitate $CdCO_3$, white, insoluble in excess of the reagents. Barium carbonate forms a complete precipitate, in the cold.—**Hydrosulphuric acid** and sulphides throw down the *sulphide*, **CdS**, yellow; insoluble in cold dilute acids, in alkalies, and in alkali sulphides or cyanides, soluble in hot and dilute sulphuric acid (compare 276).—Alkali **chromates** precipitate yellow *cadmium chromate*, from concentrated solutions only, and soluble on addition of water.—**Phosphates** form a white precipitate, readily soluble in acids; **oxalates** and oxalic acid, cadmium oxalate, white, difficultly soluble in acids. Potassic **cyanide** precipitates $CdCy_2$, white, soluble in excess of the reagent, as $(KCy)_2CdCy_2$; ferrocyanides form a white; ferricyanides, a yellow precipitate—both soluble in hydrochloric acid, and in ammonium hydrate.—**Zinc**, and especially magnesium, reduce cadmium from acid and from ammoniacal solutions, as a spongy gray precipitate.

On charcoal, with sodium carbonate, cadmium is reduced before the **blowpipe** to metallic salt, and usually vaporized and reoxidized nearly as fast as reduced, thereby forming a characteristic brown incrustation (**CdO**). This is volatile by reduction only, being driven with the reducing flame.—Cadmium oxide colors the borax **bead** yellowish while hot, colorless when cold; microcosmic salt, the same.

302. Comparison of Certain Reactions of Bismuth, Copper, and Cadmium.

Taken in solutions of their Chlorides, Nitrates, Sulphates, or Acetates.

	Bi.	Cu.	Cd.
KOH or **NaOH, in excess.**	$Bi(OH)_3$, white (289).	$Cu(OH)_2$, dark blue (273).	$Cd(OH)_2$, white (301).
NH_4OH, in excess.	$Bi(OH)_3$, white (289).	Blue solution (274).	Colorless solution.
Dilution of saturated solutions.	**BiOCl**, etc., white (288).		
Iodides.	Partial precip., in solutions not very strongly acid (295).	Partial precipitate completed by reducing agents (279).	No pre.
Sulphides.	Bi_2S_3, black, insol. in cyanide (291).	**CuS**, black, sol. in cyanide (276).	**CdS**, yellow, insolluble in cyanide.
Iron or **Zinc.**	**Bi** (spongy precip.) (297).	**Cu** (bright coating) (280).	**Cd** (gray sponge).
Sugar, KOH and **heat.**	**BiO** and **Bi** (black) (297).	$Cu_2(OH)_2$ (yellow) (280).	

LEAD.

303. Lead is a soft and malleable **metal**, of a bluish-gray color, highly lustrous on fresh surfaces, slightly lustrous after exposure; fusible at 325° C. (617° F.), and very slowly volatile by ignition. It tarnishes **in the air** at ordinary temperatures by formation of diplumbic monoxide, Pb_2O, blackish gray. Pure **water**, free from air, does not affect lead, free from oxide or hydrate, in the cold; but granulated lead slowly decomposes boiling water, with evolution of hydrogen, and formation of lead hydrate, $Pb(OH)_2$. In water containing air, the hydrate and basic carbonate are formed. This corrosion and solution are greatly promoted by nitrogenous organic matters—ammonium salts, and nitrates and nitrites—and by chlorides; hindered or prevented by carbonates, acid carbonates and sulphates. Above the melting point, lead gradually oxidizes in the air to "litharge," **PbO**.

304. Lead oxide, PbO, is a yellow powder, fusible to a reddish-yellow mass, soluble in acetic and nitric acids, in lead acetate solution, and in potassium and sodium hydrates. This oxide represents the only permanent salts of lead. Lead salts are, however, capable of oxidation, with production of less stable products (320). All the higher oxides of lead are reduced to **PbO** by ignition.

Lead forms two *basic acetates*, or "subacetates": (1) $Pb_3O_2(C_2H_3O_2)_2$, triplumbic dioxy-diacetate, or "tribasic acetate," forming the chief portion of the pharmacopœial solution of subacetate. (2) Diplumbic oxy-diacetate, $Pb_2O(C_2H_3O_2)_2$, or "dibasic acetate," of less common occurrence.

305. Triplumbic tetroxide, Pb_3O_4, "red lead" or minium, is a well-known pigment of a scarlet color. When heated, it first becomes brighter red, then turns violet. With nitric acid, it is gradually resolved into insoluble lead dioxide and lead nitrate, PbO_2 and $Pb(NO_3)_2$, the mixture acting as a strong oxidizing agent. Reducing agents, as oxalic acid, tartaric acid, or sugar, enable all the lead to be dissolved as nitrate (*a*). Hydrochloric acid in excess slowly dissolves triplumbic tetroxide, with generation of chlorine (*b*):

a. $Pb_3O_4 + 6HNO_3 + H_2C_2O_4 = 3Pb(NO_3)_2 + 4H_2O + 2CO_2$

b. $Pb_3O_4 + 8HCl = 3PbCl_2 + 2Cl + 4H_2O$

306. Lead dioxide, PbO_2, "peroxide of lead," is a brown powder. It is not soluble in nitric acid, except by aid of reducing agents. It dissolves in hydrochloric acid, with formation of lead chloride and chlorine. In acetic and phosphoric acids, with careful treatment, it forms "peroxyplumbic salts." Very strong solution of potassium hydrate, in large excess, dissolves it, with formation of "potassium plumbate," K_2PbO_3. Lead dioxide is a powerful oxidizing agent, one of the strongest known. Digested with ammonium hydrate, it forms lead nitrate and water. Triturated with one-sixth of sulphur, or tartaric acid, or sugar, it takes fire; with phosphorus, it detonates. (In study of lead dioxide as an oxidizing agent, see 835.)

307. Dilute nitric acid is the proper salifying **solvent** for lead, forming plumbic nitrate with evolution of nitric oxide. Concentrated nitric acid forms insoluble oxide. Lead does not dissolve in dilute sulphuric acid, cold or hot, or in concentrated sulphuric or hydrochloric acid, in the cold; but hot sulphuric acid, containing less than twenty-five per cent. water, forms lead sulphate, sparingly soluble in the concentrated acid; and hot concentrated hydrochloric acid forms, with evolution of hydrogen, and dissolves, a limited proportion of lead chloride. Dilute hydrochloric acid forms chloride, but dissolves little of it.

308. The oxide, and hydrate (formed in water, 303), are **soluble** in 7,000 to 10,000 parts of water, to which they give the alkaline reaction. The sulphide, carbonate, phosphate, chromate, sulphite, borate, cyanide, ferrocyanide, and tannate, are insoluble in water. The sulphate and oxalate are very slightly soluble in water; the chloride, iodide, bromide, and ferricyanide, are sparingly soluble in hot water, still more sparingly soluble in cold water. The sulphate and chloride are less soluble in dilute sulphuric and hydrochloric acids than in pure water, but much more soluble in the same acids concentrated than in water. Nitric acid increases the solubility of the sulphate and chloride in water, more and more, as the nitric acid is stronger—the salts separating again on diluting the nitric acid solution. The sulphate and chloride are insoluble in alcohol. The iodide is moderately soluble in solutions of alkaline iodides, insoluble in alcohol, decomposed by ether. The basic acetates are permanently soluble (if carbonic acid is strictly excluded). The basic nitrates are but slightly soluble in water, and are precipitated on adding solutions of potassium nitrate to solution of basic lead acetate (304).

In **analysis**, the solubility of the chloride, sparing as it is, enables lead to be separated from the other first group metals (313). As a final precipitate, in both first and second groups, the sulphate is most used. The sulphide precipitate exceeds other tests in delicacy.

309. Fixed **alkalies** precipitate, from solutions of lead salts, *lead hydrate*, $Pb(OH)_2$, white, soluble in excess of the reagents, by combination, as potassium or sodium plumbite, K_2PbO_2 (distinction from silver, mercury, bismuth, copper, cadmium). *All the precipitates of lead* hereafter given, *except the sulphide, are soluble in strong solutions of the fixed alkali hydrates.*

The alkaline solution of lead is precipitated by alkaline solutions of chromic, stannic, stannous, antimonious and arsenious oxides.

Ammonium hydrate precipitates white basic salts, insoluble in excess (distinction from silver, copper, cadmium): with the chloride, the precipitate is Pb_2OCl_2; with the nitrate, $Pb_3O_2OHNO_3$. With the acetate, in solutions of ordinary strength, excess of ammonium hydrate (free from carbonate) gives no precipitate, soluble tribasic acetate being formed.

310. Soluble **carbonates** precipitate *lead basic carbonate, white*, the carbonate and hydrate combined in proportions varied by conditions. With excess of the reagent, in concentrated solution, the precipitate consists chiefly of $Pb_3(OH)_2(CO_3)_2$. Free carbonic anhydride precipitates the basic acetate.

311. **Hydrosulphuric acid** and the **sulphides** precipitate—from neutral, acid or alkaline solutions—*lead sulphide*, **PbS**, brownish-black, insoluble in highly dilute acids, in alkalies, or alkali sulphides. Moderately dilute (15 to 25 per cent.) nitric acid dissolves the precipitate, with separation of sulphur (equation *a*); concentrated nitric acid changes it mostly to the (insoluble) lead sulphate (equation *b*)—in both cases with evolution of nitric oxide. The oxidation of the sulphur always occurs in the action of nitric acid on sulphides, in degree proportioned to the strength of acid, temperature, and duration of contact:

a. $3PbS + 8HNO_3 = 3Pb(NO_3)_2 + 3S + 2NO + 4H_2O$

b. $3PbS + 8HNO_3 = 3PbSO_4 + 8NO + 4H_2O$

In solutions too strongly acidulated, especially with hydrochloric acid, the formation of brick-red basic sulphides, as Pb_2SCl_2, interferes with perfect precipitation; in solutions excessively dilute, only a brown coloration occurs without precipitation. Lead is revealed in solutions in 100,000 parts of water, by this test.

312. Sulphuric acid and **sulphates** precipitate, from neutral or acid solutions, *lead sulphate*, $PbSO_4$, white, not chemically changed or permanently dissolved by acids, except hydrosulphuric acid, yet slightly soluble in strong acids, as more particularly stated in 308. Soluble in boiling ammonium acetate, and in the fixed alkalies. For solution by transposition into soluble salts,

see 323. Soluble in warm sodium thiosulphate solution, at temperatures not above 68° C. (154° F.); in hot solution, lead sulphite being formed, insoluble in thiosulphate; distinction and *separation from barium* sulphate, which does not dissolve in thiosulphates.

This test is from five to ten times less delicate than that with hydrosulphuric acid; but lead is quantitatively separated as a sulphate, by precipitating with sulphuric acid in presence of alcohol, and washing with alcohol. If the $PbSO_4$ is heated with K_2CrO_4, transposition takes place, and the yellow $PbCrO_4$ is formed (316). The yellow precipitate is soluble in fixed alkali hydrates, then reproduced by acetic acid. Also, excess of potassium iodide transposes lead sulphate, the yellow product (315) being a distinction of lead from barium.

313. **Hydrochloric acid** and soluble **chlorides** precipitate, from solutions not too dilute, *lead chloride*, $PbCl_2$, white. This reaction constitutes lead a member of the **FIRST GROUP**—as it also is of the second. The solubility of the precipitate is such (308), that the filtrate obtained in the cold gives marked reactions with hydrosulphuric acid, sulphuric acid, chromates, etc.; and that it can be quite accurately separated from silver chloride and mercurous chloride by much hot water. Also, small proportions of lead escape detection in the first group, while its *removal is necessarily accomplished in the second group.*

314. Soluble **Bromides** precipitate *lead bromide*, $PbBr_2$, white, soluble in water to about the same extent as the chloride; in concentrated solutions, the precipitate dissolves in excess of the potassium bromide, as $(KBr)_2PbBr_2$, which is decomposed and precipitated by dilution with water. Also soluble in hot solutions of ammonium chloride and nitrate.

315. Soluble **Iodides** precipitate *lead iodide*, PbI_2, bright yellow and crystalline, soluble in about 1,900 parts of cold or 200 of hot water; soluble in hot moderately concentrated nitric acid, and in solutions of fixed alkalies (309), not in cold hydrochloric acid; soluble in excess of the alkali iodides, by formation of double iodides—with deficient excess of potassium iodide, forming $KIPbI_2$; with superabundance of the same reagent, forming $(KI)_4PbI_2$, these double iodides requiring free alkali iodide to hold them in solution, and being partly decomposed by undue addition of water, with reprecipitation of the lead iodide. Lead iodide is not precipitated in presence of sodium citrate; alkaline acetates also hold it in solution to some extent, so that it is less perfectly precipitated from acetate than from nitrate of lead.

316. Soluble **Chromates**—both K_2CrO_4 and $K_2Cr_2O_7$—precipitate *lead chromate*, $PbCrO_4$, yellow, soluble in fixed alkali hydrates (distinction from bismuth), insoluble in chromic acid (distinction from barium), slightly soluble in acetic acid, decomposed by hydrochloric acid and by ammonium hydrate.

317. **Disodium hydrogen phosphate** precipitates trimetallic *lead phos-*

phate, $Pb_3(PO_4)_2$, white, insoluble in dilute acetic acid (compare 188), soluble in nitric acid and fixed alkalies:

$$3Pb(NO_3)_2 + 3Na_2HPO_4 = Pb_3(PO_4)_2 + 6NaNO_3 + H_3PO_4$$

And $$H_3PO_4 + Na_2HPO_4 = 2NaH_2PO_4$$

Therefore, if there is excess of phosphate, the full reaction will be:

$$3Pb(NO_3)_2 + 4Na_2HPO_4 = Pb_3(PO_4)_2 + 6NaNO_3 + 2NaH_2PO_4$$

Alkali **oxalates** precipitate *lead oxalate*, PbC_2O_4, white, insoluble in acetic acid, soluble in potassium and sodium hydrate solutions, and in nitric acid.

Alkali **sulphites**—as Na_2SO_3—precipitate *lead sulphite*, $PbSO_3$, white, less soluble in water than the sulphate, slightly soluble in sulphurous acid, decomposed by sulphuric, nitric, and hydrochloric acids.

318. Soluble **cyanides**—as **KCy**—precipitate lead cyanide, $PbCy_2$, white, soluble in a very large excess of the reagent, reprecipitated on boiling.—**Ferrocyanides**—as K_4FeCy_6—precipitate *ferrocyanide*, $Pb_2(FeCy_6)$, insoluble in dilute acids.—**Ferricyanides** form, in concentrated solutions, a dark brown precipitate, slightly soluble in water.—**Sulphocyanates** form, in concentrated solutions, a yellow crystalline precipitate of *lead sulphocyanate*, $Pb(CyS)_2$, soluble in water, decomposed on boiling, with precipitation of basic sulphocyanate, **PbOH(CyS)**, white.

319. Tannic acid precipitates solutions of lead acetate, and partly the nitrate, as yellow-gray tannate of lead, soluble in acids. Solution of lead acetate precipitates a large number—and solution of *lead subacetate* a still larger number—of **organic acids**, color substances, resins, gums, and neutral principles. Indeed, it is a rule, with few exceptions, that lead subacetate removes all organic acids (not acetic, formic, butyric, valeric, or lactic). Ammoniacal solution of lead acetate is used as a reagent, as a form of basic acetate (309).

320. Certain strong **oxidizing agents**, acting in solutions of lead salts, cause a precipitate of *lead dioxide*, PbO_2 (306). This result is obtained by saturating solution of lead acetate or alkaline solution of lead salts, or solution of lead nitrate, with gaseous **chlorine** or with strong solution of **hypochlorite**. Lead dioxide is formed by fusing lead oxide with potassium **chlorate**.

321. Lead salts are **reduced to the metallic state** by placing **zinc, iron,** magnesium, or other strongly electro-positive metal, in a solution of lead salt. The lead separates as a dark-gray, spongy mass, loosely adherent to the precipitating metal.

322. On charcoal, before the **blow-pipe,** alone or more readily with sodium carbonate, lead is reduced to malleable *globules;* while an *incrustation* of lead oxide forms around the mass—dark-yellow when hot, sulphur-yellow when cold, driven by the reducing flame, but non-volatile without reduction. The presence of this incrustation, in the reducing flame, imparts a blue *color to the outer flame.*

323. When a salt of lead is fused **with sodium carbonate on charcoal,** the acid of the lead salt combines with the sodium; but the corresponding formation of lead carbonate is prevented by the reducing power of the char-

B.P.L.
LIBRARY
PROVIDIAN

coal, which takes oxygen and forms carbonic anhydride—liberating the carbonic anhydride of the sodium carbonate, and metallic lead, thus :

$$2PbSO_4 + 2Na_2CO_3 + C = 2Pb + 2Na_2SO_4 + 3CO_2$$

In this way, lead sulphate is resolved, by transposition, into compounds soluble in water or acids. The further reducing action of the carbon, however, changes the sulphate into sulphide of sodium (677). By fusion with sodium carbonate **in a crucible**, transposition is effected without reduction, thus :

$$PbSO_4 + Na_2CO_3 = Na_2SO_4 + PbO + CO_2$$

In the decomposition in this manner of soluble salts of lead, we have the reverse of the chemical change which takes place in solution—an example of the general principle stated in the latter portion of paragraph 20. Thus, the change shown in the following equation, is essentially the reverse of the changes indicated in 313 :

$$PbCl_2 + Na_2CO_3 = 2NaCl + PbO + CO_2$$

324. With borax and microcosmic salt, strictly in the *outer flame*, lead oxide and oxidized compounds give a **bead** yellow when hot, becoming colorless when cold; due to formation of lead borate or phosphate, fused in the glass. If the least reducing action is allowed to bear on the bead, the test is spoiled, and the platinum wire is spoiled likewise. (See, under Platinum, 479.)

SILVER.

325. A metal of brilliant white lustre, very malleable, softer than copper, fusible at 1,020° C. (1,838° F.), and nearly non-volatile at furnace heat.—It is not **oxidized** by water or air at any temperature, but is oxidized by ozone, is readily attacked by chlorine, bromine, or iodine, and is soon tarnished in air containing hydrosulphuric acid, or in contact with sulphides or certain organic substances containing sulphur, by formation of silver sulphide ; also, by substances easily liberating phosphorus, as silver phosphide. As silver is easily reduced from its salts, these act as oxidizing agents of considerable force.

326. The proper **solvent** of silver is nitric acid, most efficient when about fifty per cent., but active whether concentrated or dilute—with production of nitric oxide as the chief residual product. Hot concentrated sulphuric acid forms sulphate, which is sparingly soluble ; and hot concentrated hydrochloric acid forms silver chloride, slightly soluble in the concentrated reagent, but precipitated on dilution. The fixed alkalies do not act upon silver in the wet or dry way ; hence, silver crucibles are used instead of platinum for fusion with caustic alkali. Silver, in the form of a precipitate, is very slowly acted upon by strong aqueous ammonia, dissolving as a nitride.—There is but a single series of **salts** of silver—those represented by Ag', and sometimes designated argentic salts. By reduction of silver salts, an argentous oxide, Ag_4O, and a corresponding chloride, are formed. By action of ozone on the metal, a superoxide, AgO, is produced.

327. The nitrate, acetate, and sulphate form **permanent** anhydrous crystals. The salts of silver are chiefly **colorless**, except the ortho-phosphate and arsenite, yellow ; the

arseniate, reddish-brown ; the iodide, yellow ; the bromide, yellow-white ; the sulphide, black. Normal silver salts do not redden litmus.

328. Silver forms a greater number of insoluble salts than any other metal; though, in this respect, there is but little difference between the first-group bases. The oxide, sulphide, chloride, bromide, bromate, iodide, iodate, cyanide, ferrocyanide, ferricyanide, carbonate, oxalate, phosphate, arsenite, arseniate, sulphite, and tartrate, are **insoluble** in water; the sulphate is soluble in 200 parts of cold, and less than 100 parts of boiling water. The acetate is soluble in 100 parts of water. The borate, thiosulphate, and citrate, are very sparingly soluble in water. The ammonium silver oxide and the numerous ammonium silver salts, the double cyanides, iodides, and thiosulphates of silver and alkaline metals, are soluble in water. The *chloride* is sparingly soluble in strong hydrochloric, nearly insoluble in nitric and dilute sulphuric acids; soluble, to some slight extent, in solutions of all soluble metallic chlorides (except calcium and zinc chlorides), especially soluble with sodium chloride (double chloride being formed); also soluble with certain other alkali salts, and in concentrated solution of mercuric nitrate. The *nitrate* is sparingly soluble in alcohol and in ether, and soluble in glycerine.

329. Both the oxy-salts and haloid salts of silver, which are insoluble in water, are *decomposed and dissolved* by ammonium hydrate, except the sulphide and iodide; by cold dilute nitric acid, except the chloride, bromide, iodide, bromate, iodate, and the haloids of cyanogen and its compounds; by solution of potassium cyanide, except the sulphide; and by alkali thiosulphates, almost without exception.

In **analysis,** silver is completely precipitated as a chloride, in the first group (332), and the solubility of this precipitate in ammonium hydrate separates it from the other first group bases (448). Reduction to metallic silver is sometimes employed in analysis (340).

330. The **fixed alkali hydrates** precipitate, from solutions of silver salts (in absence of citrates), *silver oxide,* Ag_2O, grayish-brown (264), insoluble in excess of the reagents; easily soluble in nitric, acetic, and sulphuric acids, and in ammonium hydrate; somewhat soluble in ammonium salts; soluble in alkali cyanides and thiosulphates ; also, soluble in about 3,000 parts of water.

Ammonium hydrate, in neutral solutions of silver nitrate, forms the same precipitate, silver oxide, very easily dissolving in excess, by formation of *ammonium silver oxide,* NH_4AgO.* In solutions containing much free acid, all precipitation is prevented by the ammonium salt formed.

The ammoniacal solution of silver is precipitated by addition of excess of fixed alkalies. This precipitate contains *fulminating silver*—a black powder, which explodes with dangerous violence by friction or by drying above ordinary temperatures. Fulminating silver may also be deposited from ammoniacal solutions of silver, on standing, and by digesting oxide of silver with strong

* This formula accords with the results of a series of volumetric determinations made by Mr. D. E. Osborne and the author (*Jour. Am. Chem. Soc.*, 1880). If silver replaces hydrogen of ammonium, the formula would be $(NH_3Ag)_2O$—the molecule of which, with a molecule of water, would make two molecules formed as given in the text. For the latter, we have :

$$AgNO_3 + 2NH_4OH = NH_4AgO + NH_4NO_3 + H_2O$$

ammonium hydrate. Its production, in the way first mentioned, is most favored by a slight excess of the fixed alkali.*

331. Hydrosulphuric acid and alkali sulphides precipitate from neutral, acid, or alkaline solutions, *silver sulphide*, Ag_2S, black, soluble in moderately concentrated nitric acid (distinction from mercury), not in solution of potassium cyanide (distinction from copper); insoluble in alkali sulphides (distinction from tin, etc.)

332. Hydrochloric acid and the soluble **chlorides** precipitate *silver chloride*, **AgCl**, white, curdy, separating on shaking the solution; turning violet to brown in the light (from formation of argentous chloride, Ag_2Cl), very easily soluble in *ammonium hydrate*, as *ammonio silver chloride*, $(NH_3)_2$-$(AgCl)_2$. The precipitate, also, is slowly soluble in concentrated solution of ammonium carbonate; and is fusible without decomposition. For solubilities of the precipitate—indicating the conditions of delicacy in the test—see 328 and 329. This precipitation is the most delicate of the ordinary tests for silver; being recognized in solution in 250,000 parts of water, and enables us wholly to remove this metal **IN THE FIRST GROUP** of bases.

333. Soluble **bromides** precipitate *silver bromide*, **AgBr**, white, with a slight yellowish tint, but slightly soluble in excess of potassium bromide, and much less easily soluble in *ammonium hydrate* than silver chloride (536).—Soluble **iodides** precipitate *silver iodide*, **AgI**, pale yellow, easily soluble in excess of the reagents by formation of double iodides, as **KIAgI**. The double iodide is decomposed by dilution with much water, and all the silver reprecipitated as iodide. The precipitate is scarcely at all soluble in *ammonium hydrate* (one part dissolving in 2,600 parts of ten per cent. solution of ammonia). Concentrated nitric acid slowly dissolves it. Regarding other solubilities of argentic bromide and iodide, see 328 and 329, and 536 and 558.

334. Potassium cyanide, or hydrocyanic acid, precipitates, from neutral or slightly acid solutions, *silver cyanide*, **AgCy**, white, quickly soluble in excess of the reagent, as potassium silver cyanide, **KCyAgCy**. By formation of these double cyanides, the various compounds of silver are rendered soluble, through treatment with alkali cyanides; also, a soluble iodo-cyanide is formed. Silver cyanide is readily soluble in ammonium hydrate, and promptly decomposed by hydrochloric acid.

335. Potassium ferrocyanide precipitates silver ferrocyanide, Ag_4FeCy_6, yellowish-white, difficultly soluble in ammonium hydrate, not decomposed by hydrochloric acid, changed by nitric acid to the ferricyanide. Exposure to the air gives it a blue tinge.—**Potassium ferricyanide** precipitates silver ferricyanide, reddish-yellow, soluble in ammonium hydrate.

* The composition of this substance, known as Berthollet's Fulminating Silver, has not been determined, but it contains nitrogen. It is distinct from the silver fulminate, $Ag_2Cy_2O_2$, represented by fulminic acid, and isomeric with cyanates.

336. Alkali **carbonates** precipitate *silver carbonate*, Ag_2CO_3, white or yellowish-white, slightly soluble in water, somewhat soluble in excess of fixed alkali carbonates, quite soluble in ammonium carbonate; soluble in nitric acid and in ammonium hydrate; changed by boiling to silver oxide. Barium carbonate does not affect solution of silver nitrate.

337. Oxalic acid, and oxalates, precipitate *silver oxalate*, $Ag_2C_2O_4$, white, slightly soluble in water, sparingly soluble by dilute nitric acid, readily soluble in solution of ammonium hydrate. It detonates when heated.

338. Disodium hydrogen phosphate precipitates trimetallic *silver ortho-phosphate*, Ag_3PO_4, yellow, soluble in dilute nitric acid, in phosphoric acid, and in ammonium hydrate; but little soluble in dilute acetic acid.—Pyrophosphates—as $Na_4P_2O_7$—precipitate silver pyrophosphate, $Ag_4P_2O_7$, white, insoluble in acetic acid, soluble in dilute nitric and phosphoric acids, and in ammonium hydrate.

339. Arseniates—as Na_3AsO_4—precipitate red-brown *silver arseniate*, Ag_3AsO_4, having the same solubilities as the ortho-phosphate.—**Arsenites**—as Na_3AsO_3—precipitate silver arsenite, Ag_3AsO_3, yellow, quickly soluble in dilute acids and in ammonium hydrate (equation at 370).

Chromates—as K_2CrO_4—precipitate silver chromate, Ag_2CrO_4, dull-red, sparingly soluble in water, not much more soluble in dilute nitric acid.

Thiosulphates—as $Na_2S_2O_3$—precipitate silver thiosulphate, $Ag_2S_2O_3$, white, very instable, and readily soluble in excess of the precipitants, by formation of double thiosulphates. That formed by sodium thiosulphate is first $NaAgS_2O_3$, with excess of the thiosulphate, $Na_4Ag_2(S_2O_3)_3$; and corresponding thiosulphates of silver and potassium are formed. By standing or heating, the precipitate turns black, as Ag_2S.

340. Silver is very easily **Reduced to the Metallic State**, from solutions of its salts, from ammoniacal solutions, and especially from its solutions in cyanides, by **reducing agents**, including the following: Zinc, copper, iron, magnesium, lead, bismuth, mercury; arsenious acid, arsenious hydride (377); antimonious hydride (411); ferrous salts, stannous salts, sulphurous acid, sugars, formic acid, certain volatile oils, and many other organic substances. The reduced silver appears as a brown-black precipitate, or in some conditions as a white lustrous coating. A bright strip of **copper**, introduced into a solution of silver nitrate, receives a lustrous silver coating (see equation in 280). A globule of **mercury**, placed in a concentrated solution of silver nitrate on a watch-glass, becomes covered with a deposit of silver *amalgam* in arborescent form—the silver tree, *arbor Dianæ*. A mass of recently precipitated silver chloride, acidulated with hydrochloric or sulphuric acid, on introducing a piece of **zinc** without agitation, is steadily reduced throughout, as shown by the advancing boundary of dark brown color in the mass. Silver oxide, as recently precipitated by fixed alkali, or silver chloride with fixed alkali, treated with cane **sugar** or grape sugar, turns brownish black, as precipitated silver. The same form of precipitate is obtained by the larger number of reducing agents. By a *gradual* reduction of the silver with certain reagents, it is obtained as a bright *silver coating* upon the inner surface of the test-tube, or other glass vessel. A somewhat dilute solution of ammonio nitrate of silver, treated with a dilute alcoholic solution of oils of cloves and cassia —the latter solution not in excess—gives this result. The coating is also obtained by adding to solution of silver nitrate a very little aqueous solution of chloral hydrate, and then a slight excess of ammonia; the ammonium formiate, gradually produced by decomposition of the chloral with alkali, deoxidizes the ammonio silver nitrate. A silver deposit on glass may sometimes be made to assume the form of a compact and lustrous coating, by

rubbing with a glass rod. In these deoxidations, generally, the nitric acid radical of silver nitrate is not decomposed, but nitric acid is left.

$$2AgNO_3 + H_2O = 2Ag + 2HNO_3 + O$$

See, as an example, the statement of the reaction between arsenious hydride and silver nitrate, under Arsenious Acid (377).

Light decomposes most compounds of silver, with blackening from formation of metallic silver or of argentous oxide, Ag_4O, or of both. The nitrate in crystal or pure water solution, the phosphate, iodide, and cyanide, are not decomposed by light alone; but light greatly hastens their decomposition by organic substances, or other reducing agents—as of solution of silver nitrate in rain-water, or written as an ink upon organic fabrics.

341. Silver nitrate and chloride fuse undecomposed, but decompose at a higher heat. Most silver compounds, heated in the **glass-tube**, leave a metallic residue. On **Charcoal**, with sodium carbonate, silver is reduced from all its compounds in the blow-pipe flame, attested by a bright malleable globule. Lead and zinc, and elements more volatile, may be separated from silver by their gradual vaporization under the blow-pipe. Copper and iron are removed along with larger quantities of lead, previously added for this purpose, either as metallic lead or by reduction from litharge. (See descriptions of *Cupellation*, in works on general chemistry, and more fully in works on assaying of precious metals.)

MERCURY.

342. A tin-white, lustrous **metal,** liquid at temperatures between –40° and 360° C. (–40° and 680° F.), slightly volatile at ordinary temperatures. Divided in globules invisible to the unaided eye, and separated by minute films of liquid or solid foreign matter, mercury appears as a dark gray powder, exceedingly mobile. It is not **oxidized** by agitation with air or oxygen—the tarnish acquired on the surface of commercial mercury, by exposure to the atmosphere, being due to intermixture of foreign metals; but by agitation with water, or with various substances, the metal is "extinguished," or divided to the gray pulverulent form, which contains some mercurous oxide when so prepared. Also, the gray pulverulent mercury is precipitated by reduction from salts in solution. Aqueous solutions of alkali chlorides, with access of the air, gradually act upon mercury by formation of mercuric chloride. Solution of potassium permanganate oxidizes mercury—forming mercurous oxide, manganic hydrate, and potassium hydrate.

343. The most effective **solvent** of mercury is **nitric acid.** It dissolves readily in the dilute acid with heat, or in the cold, if nitrous acid is present; with the strong acid, heat is soon generated; and with considerable quantities of material, the action acquires an explosive violence. At ordinary temperatures, dilute nitric acid, when applied in slight excess, produces chiefly normal mercurous nitrate, but when the mercury is in excess, more or less of basic mercurous nitrate is formed; hot dilute nitric acid, in excess, forms chiefly mercuric nitrate; when the mercury is in excess, both basic mercurous and basic mercuric nitrates are formed—in all cases, chiefly nitric oxide gas is generated. **Chlorine**—in aqueous solution, or formed in nitro-hydrochloric acid—dissolves mercury slowly, to mercuric chloride. **Hydrochloric acid**, at ordinary temperatures, does not affect mercury; and the concentrated acid, by long boiling, scarcely attacks it. **Bromine** and **iodine** promptly unite with mercury. Dilute **sulphuric acid** does not act upon mercury; but the concentrated acid, when heated, dissolves it with moderate rapidity, evolving sulphurous anhydride.

344. Mercury forms two well-marked oxides—Hg_2O, black, and HgO, red—and two corresponding **classes of salts**—the mercurous compounds being permanent in the air, but changed by powerful oxidizing agents to mercuric compounds. The latter are somewhat more stable, but act as oxidizing agents in many relations. Mercury as a noble metal is not strongly electro-positive; and many reducing agents change mercuric compounds, first to mercurous combinations, and then to metallic mercury.

Solutions of mercurous and mercuric salts redden **litmus.** Mercuric chloride is **permanent**; nitrate, deliquescent.

345. MERCUROUS compounds, of ordinary occurrence, are **insoluble** in water, except the normal nitrate; the sulphate and the acetate are sparingly soluble (that is, in 300 to 600 parts of water). And these require acidulated water for their full solution; becoming *decomposed by* **water,** at a certain degree of dilution, with precipitation of basic salts (261).

Mercurous chloride is very slowly soluble by cold concentrated solutions of alkali chlorides, somewhat more rapidly when heated, the solution being due to formation of mercuric chloride and mercury. Dilute hydrochloric acid, at ordinary temperatures, fails to dissolve mercurous chloride; but when heated it gradually causes the formation of mercuric chloride and mercury, the action being very slow with dilute acid, tolerably rapid with concentrated acid. In presence of certain organic substances, the resolution into mercuric chloride and mercury takes place at 38° to 40° C. (100° F.) Free **chlorine,** and **nitric acid,** quickly dissolve mercurous chloride, as mercuric salt.

In **analysis,** mercurous compounds are precipitated, from solution, as chloride, in the first group (350), and this precipitate is distinguished from others in the group, by blackening with ammonium hydrate (448). The identification of mercury, by reduction to metallic state, is the same as with mercuric compounds (363).

346. Fixed alkali hydrates precipitate, from solutions of mercurous salts, *mercurous oxide*, Hg_2O (264), black, insoluble in alkalies.

347. Solution of **ammonium hydrate** produces black precipitates; that from solution of mercurous nitrate being $(NH_2Hg_2)NO_3$, nitrogen dihydrogen dimercurous nitrate,* black, insoluble in alkalies, soluble in acids:

$$2HgNO_3 + 2NH_4HO = NH_2Hg_2NO_3 + NH_4NO_3 + 2H_2O$$

Mercurous chloride, white, is changed by ammonium hydrate to $(NH_2Hg_2)Cl$, nitrogen dihydrogen dimercurous chloride, or dimercurous ammonium chloride,

* The compounds produced by action of ammonium hydrate on mercury compounds are considered as substitutions of **Hg** for a certain number of atoms of **H** in NH_4 (ammonium). The substitutions formed from *mercurous* compounds contain (200 parts by weight or) one atom of **Hg** (acting as a monad) for each atom (1 part) of **H** displaced; they are termed mercurous-ammoniums; mercurosammonium being NH_3Hg; di-mercurosammonium, NH_2Hg_2; tri-mercurosammonium, $NHHg_3$, etc. The substitutions formed in ammonium by mercury from *mercuric* compounds contain one atom of **Hg** (acting as a dyad) for two atoms of **H** displaced; they are designated as mercurammoniums; mercurammonium being $(NH_3)_2Hg$; di-mercurammonium, NH_2Hg; tri-mercurammonium, $(NH)_2Hg_3$; tetra-mercuramonium, NHg_2.

black (distinction from lead), decomposed by acids, insoluble in ammonium hydrate (distinction from silver):

$$Hg_2Cl_2 + 2NH_4HO = NH_2Hg_2Cl + NH_4Cl + 2H_2O$$

348. Solutions of the **carbonates** of the fixed alkali metals precipitate an instable mercurous carbonate, Hg_2CO_3, gray, blackening to basic carbonate and oxide when heated. Ammonium carbonate reacts like ammonium hydrate (347). Barium carbonate precipitates mercurous salts, in the cold.

349. **Hydrosulphuric acid,** and soluble sulphides, precipitate *mercurous sulphide*, Hg_2S, black, containing variable proportions of HgS and Hg, into which it is soon resolved without change of color. The precipitate is insoluble in nitric acid, hydrochloric acid, or ammonium sulphide. The sulphides of the metals of the fixed alkalies—Na_2S and K_2S—slowly change mercurous to mercuric sulphide, and sparingly dissolve it (359, equation *b*).

350. **Hydrochloric acid** and soluble chlorides form a white precipitate of *mercurous chloride*, Hg_2Cl_2, "calomel"—placing the mercurous base **IN THE FIRST GROUP.** For relations of the precipitate to solvents, see 345; to ammonium hydrate, see 347; fixed alkalies blacken it by formation of Hg_2O (346).

351. Soluble **bromides** precipitate *mercurous bromide*, Hg_2Br_2, yellowish white, insoluble in water and in alcohol, insoluble in dilute nitric acid.

352. Soluble **iodides** precipitate *mercurous iodide*, Hg_2I_2, greenish-yellow—"the green iodide of mercury." The precipitate from mercurous nitrate contains more or less mercuric iodide; that from the acetate is nearly pure Hg_2I_2.

Mercurous iodide is nearly insoluble in water, insoluble in alcohol (distinction from mercuric iodide), somewhat soluble in ether, slowly soluble in part by aqueous solutions of alkali iodides (excess of the precipitants), being first decomposed to mercuric iodide and mercury, which last remains undissolved:

$$Hg_2I_2 + 2KI = Hg + (KI)_2HgI_2$$

Ammonium hydrate solution slowly and partially dissolves mercurous iodide.

By sublimation, and to some extent by exposure to light, mercurous iodide is changed to *mercuroso-mercuric iodide*, $HgI.HgI_2$, yellow—with separation of metallic mercury. When the precipitate by iodide of potassium, in solution of mercurous nitrate, is made in very dilute solutions or is allowed to stand for some time, it consists chiefly of this—"the yellow iodide of mercury." It is strictly insoluble in alcohol; melts and sublimes undecomposed, and is affected by alkali iodides like mercurous iodide.

353. Alkali **cyanides**, also hydrocyanic acid, resolve mercurous salts into metallic mercury, a gray precipitate, and mercuric cyanide, which remains in solution.—**Ferrocyanides** form a white, gelatinous; **ferricyanides**, a red-brown precipitate.

Alkali **phosphates**—as Na_2HPO_4—precipitate the white *mercurous phosphate*, Hg_3PO_4, when the reagent is added in excess; the yellow mercurous phosphate-nitrate, $Hg_3PO_4.HgNO_3$, when mercurous nitrate is in excess.—**Chromates** precipitate the orange-yellow *mercurous chromate*, basic; changed by dilute nitric acid to the normal Hg_2CrO_4; by strong nitric acid changed to mercuric chromate, and dissolved.—Oxalic

acid and **oxalates** precipitate the white *mercurous oxalate*, $Hg_2C_2O_4$, slightly soluble in dilute nitric acid.

Soluble **sulphates** precipitate, from solutions not dilute, the white *mercurous sulphate*, Hg_2SO_4, sparingly soluble in water (345); decomposed by boiling water with precipitation of a basic sulphate; more soluble in dilute nitric acid; blackened by ammonium hydrate and fixed alkalies (distinction from other sparingly soluble sulphates).

354. Mercurous compounds are **reduced** to metal by the same reducing agents that reduce mercuric compounds to metal; but not by all the reducing agents capable of converting mercuric to mercurous combinations, as more fully specified in 362. As to oxidation of mercurous compounds, see 837.—The reactions **in the dry way** are nearly the same as those for mercuric compounds (363).

355. MERCURIC oxide, sulphide, iodide, iodate, basic carbonate, oxalate, phosphate, arseniate, arsenite, ferrocyanide, and tartrate, are **insoluble** in water. The bromide is soluble in 250 parts of cold, or one-tenth that proportion of boiling water. The acetate and cyanide are freely, the chromate and citrate sparingly, soluble in water. The double iodides of mercury, and the metals of the alkalies and alkaline earths, are soluble in water—that is, mercuric iodide is soluble in aqueous solutions of alkali iodides. The double bromides dissolve in a smaller proportion of water than the bromide. Except the chloride, the ordinary mercuric salts which are soluble in water are so only by presence of free acid, being partially *decomposed by water*, with separation of basic salts (261). In work with solution of mercuric nitrate, some of the reactions are modified by the free acid, always present.—Mercuric sulphate is soluble in very dilute sulphuric acid.—The *chloride* is soluble in about 12 parts of cold, or two to three parts of boiling water; freely soluble in alcohol and in ether.

In **analysis,** the second group precipitate of mercury sulphide is separated by its insolubility in nitric acid (464). The final form, in determination of mercury, is usually the metallic state (362 *a*, or 363).

356. Solutions of the **fixed alkali hydrates,** added short of saturation, to solutions of mercuric salts, precipitate reddish-brown *basic salts;* when the reagent is added to supersaturation, the orange-yellow *mercuric oxide*, **HgO,** is precipitated. Prepared in the dry way, mercuric oxide is obtained red—the "red precipitate" of the shops. From very acid solutions, the precipitate is incomplete or does not form at all, owing to its solubility in alkali salts. It is very slightly soluble in water. In presence of an ammonium salt, the white precipitate (357) is formed. Certain organic acids interfere with the precipitation.

357. Ammonium hydrate produces a "white precipitate," recognizable in very dilute solutions (compare 59); that with neutral solution of mercuric chloride being $(NH_2Hg)Cl$, nitrogen dihydrogen mercuric chloride, or dimercurammonium chloride (*a*)—(347); that with hot dilute solution of mercuric nitrate and excess of ammonia being $(NHg_2)NO_3$, nitrogen dimercuric nitrate

(*b*). The precipitates are easily soluble in hydrochloric acid; sparingly soluble in strong ammonium hydrate, which should not be used in excess in precipitation. They are also more or less soluble in ammonium salts, and especially in ammonium nitrate. Therefore, the precipitation by ammonium hydrate is always in some degree incomplete; and that of the acid mercuric nitrate is decidedly diminished, and in very dilute solutions prevented altogether, by the ammonium salt formed in the reaction (as shown in equations *a* and *b*). A soluble combination of ammonium chloride with mercuric chloride, $(NH_4Cl)_2$-$HgCl_2$, or ammonium mercuric chloride, called "sal alembroth," is not precipitated by ammonium hydrate, but potassium hydrate precipitates therefrom the white mercurammonium chloride, $(N_2H_6Hg)Cl_2$ (*c*).

a. $HgCl_2 + 2NH_4OH = (NH_2Hg)Cl + NH_4Cl + 2H_2O$

b. $2Hg(NO_3)_2 + 4NH_4OH = (NHg_2)NO_3 + 3NH_4NO_3 + 4H_2O$

c. $(NH_4Cl)_2HgCl_2 + 2KOH = ([NH_3]_2Hg)Cl_2 + 2KCl + 2H_2O$

Ammonium carbonate reacts like ammonium hydrate (compare 59).

358. Potassium and sodium **carbonates** precipitate first red-brown *basic salts*, which, by excess of the precipitants with heat, are converted into the yellow mercuric oxide. The basic salt formed with mercuric chloride is an oxy-chloride, $HgCl_2.(HgO)_{2,\ 3,\ or\ 4}$; with mercuric nitrate, a basic carbonate, $(HgO)_3HgCO_3$ or $(HgO)_4CO_2$.—**Barium carbonate** precipitates a basic salt in the cold, from the nitrate, but not from the chloride.

359. Hydrosulphuric acid, gradually added to solutions of mercuric salts, forms at first a white precipitate, soluble in acids and in excess of the mercuric salt; by further additions of the reagent, the precipitate becomes yellow-orange, then brown, and finally black, insoluble in hydrochloric or nitric acid. This progressive variation of color is characteristic of mercury, and is also produced by **ammonium sulphide.** The final and stable precipitate is *mercuric sulphide*, **HgS**; the lighter colored precipitates consist of unions of the original mercuric salt with mercuric sulphide, as $HgCl_2.HgS$, the proportions of **HgS** being greater with the darker precipitates. When sublimed and triturated, the black mercuric sulphide is converted to the red (vermilion), without chemical change.

Mercuric sulphide is soluble by free chlorine (nitro-hydrochloric acid) (*a*); not affected by nitric acid (distinction from all other metallic sulphides) or by hydrochloric acid; insoluble in ammonium sulphide (distinction from tin, antimony, arsenic); somewhat soluble in solutions of sulphides of potassium and sodium, by formation of double sulphides (*b*) soluble in alkali hydrates or sulphide solutions, but decomposed by pure water; also, slowly and partially soluble in fixed alkalies, by formation of alkaline sulphides (*c*).

a. $HgS + Cl_2 = HgCl_2 + S$

b. $HgS + K_2S = K_2S.HgS$

c. $2HgS + 2KOH = K_2S.HgS + HgO + H_2O$

360. Soluble **bromides** precipitate, from concentrated solution of mercuric nitrate (not from the chloride), the white *mercuric bromide*, $HgBr_2$, soluble in water (355), the solution giving the mercuric reactions, and being precipitable by reduction (362) to mercurous bromide (351). The precipitate is decomposed by strong or hot nitric acid.

Soluble **iodides** precipitate *mercuric iodide*, HgI_2, first reddish-yellow, then red; very slightly soluble in water, soluble in concentrated nitric and hydrochloric acids; quickly soluble in solutions of the iodides of all the more positive metals—that is, in excess of its precipitants, by formation of soluble *double iodides;* as $(KI)_2HgI_2$ variable to $KI.HgI_2$.*

The *potassium-mercuric iodide* (sometimes designated the iodo-hydrargyrate of potassium) is precipitated by **ammonium hydrate,** and by the alkaloids (see Nessler's Test, 58). Dilute acids precipitate the mercuric iodide.

361. Soluble normal **chromates** precipitate, from very concentrated solutions, basic mercuric chromates, orange yellow to red; considerably soluble in water, more soluble in solution of mercuric chloride or nitrate. Soluble **phosphates,** as Na_2HPO_4, precipitate **mercuric phosphate,** $Hg_3(PO_4)_2$, white, soluble in acids, including phosphoric acid, and in ammonium salts. Soluble **oxalates,** and oxalic acid, precipitate—from the nitrate, but not from the chloride—*mercuric oxalate,* HgC_2O_4, white, readily soluble in dilute hydrochloric acid, difficultly soluble in nitric acid. **Potassium Ferrocyanide** precipitates mercuric ferrocyanide, white, becoming blue on standing.

362. Reducing agents precipitate, from the solutions of mercuric and mercurous nitrates, *dark-gray* **Hg** (342); from solution of mercuric chloride, or in presence of chlorides, *first the white,* Hg_2Cl_2 (350), *then gray* **Hg.** Strong acidulation with nitric acid interferes with the reduction, and heating promotes it. By digestion with hot concentrated hydrochloric acid—and a little solution of stannous chloride—the gray precipitate of divided mercury is converted into liquid globules of metallic lustre. This somewhat tardy result is hastened by trituration with a glass rod in the test-tube.

The reducing agent most frequently employed is **stannous chloride** (*a*). Boiling solution of sulphurous acid (*b*), or thiosulphates (*c*), effect the reduction. A clean strip of **copper,** placed in a slightly acid solution of a salt of mercury, becomes coated with metallic mercury, and when gently rubbed with cloth or paper presents the tin-white lustre of the metal (*d*), the coating being driven off by heat. Zinc and iron, also, reduce mercury, and from mercuric chloride

* A hot concentrated solution of potassium iodide dissolves $3HgI_2$ for every $2KI$. The first crystals from this solution are $KI.HgI_2$. These are decomposed by pure water, and require a little free iodide for perfect water solution, but they are soluble in alcohol and in ether.

or in presence of chlorides, first precipitate calomel. Formic acid reduces mercuric to mercurous chloride, and in the cold does not effect further reduction. Dry mercuric chloride, moistened with alcohol, is reduced by metallic *iron;* a bright strip of which is corroded soon after immersion into the powder tested (a delicate distinction from mercurous chloride). Further, see 838.

a. $2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$

$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4$

Or: $HgCl_2 + SnCl_2 = Hg + SnCl_4$

Also: $2Hg(NO_3)_2 + SnCl_2 = Hg_2Cl_2 + Sn(NO_3)_4$

b. $HgCl_2 + H_2SO_3 + H_2O = Hg + H_2SO_4 + 2HCl$

c. $2HgCl_2 + 2Na_2S_2O_3 = Hg_2Cl_2 + 2NaCl + Na_2S_4O_6$

Or: $HgCl_2 + 2Na_2S_2O_3 = Hg + 2NaCl + Na_2S_4O_6$

d. $2HgNO_3 + Cu = 2Hg + Cu(NO_3)_2$ (compare 280).

363. All compounds of mercury, in glass tubes or on charcoal, are quickly *volatile* before the **blow-pipe.** Mercurous chloride and bromide and mercuric chloride and iodide sublime (in glass tubes) *undecomposed*—the sublimate condensing (in the cold part of the tube) without change. Most other compounds of mercury are decomposed by vaporization, and give a sublimate of metallic mercury (mixed with sulphur, if from the sulphide, etc.) *All* compounds of mercury, dry and intimately mixed with dry **sodium carbonate,** and heated in a glass tube closed at one end, give a sublimate of metallic mercury as a gray mirror coat on the inner surface of the cold part of the tube. Under the magnifier, the coating is seen to consist of globules, and by gently rubbing with a glass rod or a wire, globules visible to the unaided eye are obtained.

364. Comparison of Certain Reactions of First Group Metals,

Taken in Solution of their Nitrates or Acetates.

	Pb.	Ag.	Hg_2''	Hg''
KOH or **NaOH in excess**	Solution (309).	Ag_2O, grayish brown (330).	Hg_2O, black (346).	HgO, yellow to red (356).
NH_4OH **in excess**	White precipitate. Not formed in the acetate (309).	Solution (330).	$(NH_2Hg_2)NO_3$, black (347).	$(NHg_2)NO_3$, white ; $(NH_2Hg)Cl$, white (357).
Chlorides	$PbCl_2$, sparingly soluble in water, more freely if hot (313).	AgCl, white (332).	Hg_2Cl_2, white, dissolved by oxidizing acids (350).	Solution.
Bromides	$PbBr_2$, slightly soluble in water (314).	AgBr, pale yellowish-white (333).	Hg_2Br_2, yellowish-white (351).	(360).
Iodides	PbI_2, orange-yellow, sparingly soluble in alkali iodides (315).	AgI, pale-yellow, freely soluble in alkali iodides (333).	Hg_2I_2, yellowish-green, decomposed by alkali iodides (352)	HgI_2, red, freely soluble in alkali iodides (361).
H_2SO_4 and **Sulphates**	$PbSO_4$, least soluble sulphate except barium (312).	No precip., except in concentrated solutions (328).	No precipitate in dilute solutions (353).	Solution requires a little free acid (355).
Chromates	$PbCrO_4$, yellow (315).	Ag_2CrO_4, purple-red, not formed in dilute solutions (339).	Hg_2CrO_4, orange-yellow (353).	Precipitate only in concent. solutions (361).
Zinc	Pb (321).	Ag (340).	Hg (362).	Hg_2'' salts, then Hg (362).
Lead	. . . . .	Ag.	Hg.	Hg_2'' salts, then Hg (362).
Mercury	. . . . .	Ag.		
Stannous Salts	. . . . .	Ag.	Hg.	Hg_2'' salts, then Hg.

ARSENIC (ARSENICUM).

365. A steel-gray, lustrous, brittle, and easily pulverizable non-metallic element, vaporizing directly from the solid state at 356° C. (673° F.) in closed vessels; the vapor being colorless, with a strong and oppressive alliaceous odor. It is slowly **oxidized** in moist (not in dry) air at ordinary temperatures, with formation of the black "suboxide," "fly-powder"; when heated in the air, it burns with a bluish flame, and becomes the white arsenious anhydride, As_2O_3. It readily combines with chlorine and bromine upon contact, and with iodine and sulphur by aid of heat. It is not attacked by aqueous hydrochloric acid at ordinary temperatures, and but slightly when hot and concentrated and with air; it is slowly oxidized to arsenic acid by hot concentrated sulphuric acid, or more readily by nitric acid; but its proper **solvent** is nitro-hydrochloric acid, or chlorine with water, by which it is oxidized to arsenic acid with violent rapidity (*a*). Hot solution of potassium or sodium hydrate dissolves it as arsenite (*b*):

a. $2As + 10Cl + 8H_2O = 2H_3AsO_4 + 10HCl$

b. $As + 3KOH = K_3AsO_3 + 3H$

Arsenic forms two important **oxides,** both acidulous (260); *arsenious anhydride,* As'''_2O_3, representing a series of arsenious compounds and arsenites of metals, but forming no acid existing separate from water; and *arsenic* anhydride, $As^v_2O_5$, forming arseniates of metals, and arsenic acids, and representing other arsenic compounds. Both these classes of compounds possess considerable stability; the arsenious bodies acting as efficient reducing agents, and the arsenic substances, with less activity, as oxidizing agents.

366. ARSENIOUS anhydride—having both crystalline and amorphous modifications—is very slowly and sparingly soluble in cold water, much more quickly but quite sparingly soluble in hot water, the solution feebly reddening litmus; freely soluble in hydrochloric acid, and somewhat soluble in sulphuric acid without combination; readily soluble in alkali hydrates with combination (equation *a*); slightly soluble in alcohol, and soluble in glycerine.—*Arsenious chloride* is wholly decomposed by water, with formation of arsenious oxide and hydrochloric acid (equation *b*), *arsenious sulphide* is very slightly soluble in pure water, insoluble in acidulated water, but soluble by combination in solutions of alkalies (*c*), alkaline carbonates (*d*), and alkaline sulphides (*e*).—*Arsenites* of the alkali metals are soluble in water; of the alkaline-earth metals sparingly soluble, of magnesium insoluble; of all other metals, insoluble. The arsenites are decomposed—and, except those of first group metals, dissolved—by hydrochloric acid, and are decomposed and dissolved by nitric acid, without exception:

a. $As_2O_3 + 6KOH = 2K_3AsO_3 + 3H_2O$ (with excess of alkali).

b. $AsCl_3 + 3H_2O = H_3AsO_3 + 3HCl$

c. $As_2S_3 + 6KOH = K_3AsO_3 + K_3AsS_3 + 3H_2O$

d. $As_2S_3 + 3(NH_4)_2CO_3 = (NH_4)_3AsO_3 + (NH_4)_3AsS_3 + 3CO_2$

e. $As_2S_3 + 3(NH_4)_2S = 2(NH_4)_3AsS_3$ (variable).*

* Dibasic and monobasic, as well as tribasic sulpharsenites are formed in different conditions. According to NILSSON (*Bericht. d. deut. chem. Ges.*, IV., 989; *Jour. Chem. Soc.*, X., 1872, 599), $(NH_4)HS$ always dissolves As_2S_3 as $(NH_4)_2S.(As_2S_3)_3$. With yellow ammonium sulphide, the excess of **S** is left as a residue. When arsenious oxide, As_2O_3, is fully *saturated* with alkalies, it forms *tri-metallic* oxy-salts, the typical **arsenites**—as K_3AsO_3, or $(NH_4)_3AsO_3$ (according to equation *a*); but when partially saturated with alkalies, *di-metallic* or monometallic arsenites may be formed—as K_2HAsO_3 or KH_2AsO_3.

In **analysis**, the second group precipitate of arsenious sulphide is separated, with antimony and tin, by solution with ammonium sulphide (455). The final determination, and separation from antimony and tin, are usually effected by production of arsenious hydride gas (Marsh's test) (373 and 377).

367. **Alkali hydrates and carbonates** do not precipitate arsenious compounds from solution; whereby arsenic is distinguished from the bases.

368. **Hydrosulphuric acid** precipitates the lemon-yellow *arsenious sulphide*, As_2S_3. The precipitate forms promptly in acidulated solutions, the most perfectly with hydrochloric acidulation; being complete even in strong hydrochloric acid solution, but diminished by too strong nitric acid. It forms slowly in simple aqueous solution of arsenious acid, as a color rather than a precipitate; being slightly soluble in pure water, but insoluble in acidulated water. It is not formed in solutions of alkali arsenites, except by acidulation. Citric acid and other *organic* substances hinder, but, in presence of much hydrochloric acid, do not wholly prevent its formation. Alkali **sulphides** produce, and by further addition dissolve, the precipitate.

The *arsenious sulphide is soluble* in solutions of alkali hydrates, carbonates, and sulphides, as severally explained in 366. From all these alkaline sulphidic solutions, acids reprecipitate the sulphide (*a* and *b*). By its solubility in solution of **ammonium sulphide**, it is separated with antimony and tin from the other members of group second; and by its solubility in solution of **ammonium carbonate**, it is approximately separated from antimony and tin, in a process of separation which has been in common use (given in 459):

a. $2(NH_4)_3AsS_3 + 6HCl = As_2S_3 + 6NH_4Cl + 3H_2S$

b. $(NH_4)_3AsO_3 + (NH_4)_3AsS_3 + 6HCl = As_2S_3 + 6NH_4Cl + 3H_2O$

The color of the As_2S_3 distinguishes it from **S**, derived thus:

c. $(NH_4)_2S_2 + 2HCl = S + 2NH_4Cl + H_2S$

The *arsenious sulphide* is also soluble in solutions of alkali **sulphites** with free sulphurous acid (distinction, and a method of separation from antimony and tin, 461):

d. $2As_2S_3 + 16KHSO_3 = 4KAsO_2 + 6K_2S_2O_3 + 3S + 7SO_2 + 8H_2O$

Like metalloidal arsenic, the *arsenious sulphide* is insoluble in **hydrochloric acid**—another means of separation from antimony and tin. It dissolves by **nitric acid**, and by free **chlorine** or nitro-hydrochloric acid, as *arsenic anhydride*, As_2O_5, or arsenic acid, H_3AsO_4,—(equations *e* and *f*. Compare equation *a*, 365). Arsenious sulphide is not changed to arsenious oxide by any solvents. By **nitric acid**, **As** can be separated from **Sb**, **Sn**, **Bi**, etc. (460):

e. $As_2S_3 + 10Cl + 8H_2O = 2H_3AsO_4 + 3S + 10HCl$

f. $3As_2S_3 + 10HNO_3 + 4H_2O = 6H_3AsO_4 + 9S + 10NO$

369. **Thiosulphates**—as $Na_2S_2O_3$—also precipitate, from boiling hydrochloric acid solution of arsenious acid, the *arsenious sulphide* (distinction from tin, 462):

$$2H_3AsO_3 + 3Na_2S_2O_3 = As_2S_3 + 3Na_2SO_4 + 3H_2O$$

370. **Silver nitrate** solution precipitates from neutral solutions of arsenites, or ammonio silver nitrate* from water solution of arsenious oxide, *silver arsenite*, Ag_3AsO_3, yellow, readily soluble in dilute acids or in ammonium hydrate or ammonium salts (339):

$$(NH_4)_3AsO_3 + 3AgNO_3 = Ag_3AsO_3 + 3NH_4NO_3$$

$$\textit{Or } H_3AsO_3 + 3AgNO_3 + 3NH_4OH = Ag_3AsO_3 + 3NH_4NO_3 + 3H_2O$$

371. **Copper sulphate** solution precipitates from solutions of neutral arsenites, or ammonio copper sulphate (prepared as directed in note under 370), precipitates from water solution of arsenious oxide, the green *copper arsenite*, $CuHAsO_3$ or $Cu_3(AsO_3)_2$ (Scheele's green), soluble in ammonium hydrate and in dilute acids. **Copper acetate** in boiling solution precipitates the green *copper aceto-arsenite* $(CuOAs_2O_3)_3Cu(C_2H_3O_2)_2$ (Schweinfurt green), soluble in ammonium hydrate and in acids. Both these colors are often designated as Paris green (277). For the reaction of Copper Salts with fixed alkali hydrate, see 385 *d*.

372. In general, solutions of *arsenites* are precipitated by solutions of normal **salts of the metals**, except those of the alkalies, and barium, strontium, and calcium (366). Normal magnesium salts form a white precipitate of magnesium arsenite. The precipitate is soluble in ammonium hydrate and ammonium chloride (distinction from arseniates).

Ferric salts precipitate from arsenites, and **recent ferric hydrate** (*used as an antidote*), forms with arsenious anhydride, variable *basic ferric arsenites*, scarcely soluble in acetic acid, soluble in hydrochloric acid. Water slowly and sparingly dissolves from the precipitate the arsenious anhydride; but a large excess of the ferric hydrate holds nearly all the arsenic insoluble. To some extent, the basic ferric arsenites are transposed into basic ferrous arseniates, insoluble in water, in accordance with the reducing power of arsenious oxide.

373. Arsenic is **reduced** to the elemental state by several methods of great analytical importance.

By the action of **hydrogen** generated in acid solution (Marsh's Method) it is reduced from all its soluble compounds, when it enters into a combination with hydrogen as *arsenious hydride*, AsH_3, gaseous. The latter can be identified by numerous reactions, and from it the arsenic can readily be obtained free.

The hydrogen is generated by **sulphuric acid** diluted with 6 to 8 parts water, and **zinc** (both free from arsenic). Compare 233 *a*. The hydrogen re-

* Prepared by adding ammonium hydrate to the solution of silver nitrate, till the precipitate at first produced is *nearly* all redissolved.

moves the oxygen, from either oxide of arsenic, by forming water, and then combines with the arsenic; two atoms of hydrogen taking the place of one atom of oxygen:

$$As_2O_3 + 12H = 3H_2O + 2AsH_3$$

or, including the zinc and sulphuric acid:

$$H_3AsO_3 + 3(Zn + H_2SO_4) = 3ZnSO_4 + 3H_2O + AsH_3$$

$$H_3AsO_4 + 4(Zn + H_2SO_4) = 4ZnSO_4 + 4H_2O + AsH_3$$

It will be seen that arsenious hydride cannot be formed in presence of free chlorine or other oxidizing agents, such as nitric acid, nitrates, chlorates, and hypochlorites. Sulphur and sulphites interfere; also mercury salts (by amalgamation of the zinc), and *most organic substances.* Free arsenic and arsenious sulphides are not acted on by the nascent hydrogen. With zinc, strong **potassium hydrate** or **sodium hydrate** may be used instead of acid, the action being slower. **Sodium amalgam** alone, in solutions neutral, acid, or alkaline, causes an abundant generation of arsenious hydride if arsenic is present. In the test made by sodium amalgam, in alkaline solution, cane sugar, and some other organic bodies do not interfere.

The generation of arsenious hydride, by metallic **magnesium,** when done in strong solution of **ammonium chloride,** is a separation from antimony. The solution may be neutral or alkaline, but, for the separation, not acid.

Metallic **aluminium,** in strong potassium hydrate solution, on warming, generates arsenious hydride from arsenical compounds (distinction and separation from antimony).

Phosphates interfere with the tests, in alkaline solutions, by sodium amalgam, magnesium, and aluminium, causing formation of phosphorous hydride and blackening of the silver solution.

374. *Arsenious hydride* (arsine) burns when a stream of it is **ignited** where it enters the air, and explodes when its mixture with air is ignited, like other combustible gases. It burns in a stream, with a somewhat luminous and slightly bluish flame (distinction from hydrogen); the hydrogen being first oxidized, and the liberated arsenic becoming incandescent, and then undergoing oxidation; the vapors of water and arsenious anhydride passing into the air (*a*). If a piece of **cold porcelain** is held in the flame, the reduction of temperature prevents the oxidation of the arsenic, which is deposited in dark steel-gray *spots*, adherent to the porcelain, about which a little of the water of combustion condenses (*b*):

$$a.\quad 2AsH_3 + 6O = As_2O_3 + 3H_2O$$

$$b.\quad 2AsH_3 + 3O = 2As + 3H_2O$$

In many particulars above mentioned, the combustion of arsenious hydride resembles that of the hydrocarbons of illuminating gas.

Arsenious hydride is an exceedingly poisonous substance; the inhalation of the unmixed gas being quickly fatal. Its dissemination in the air of the laboratory, even in the small portions which are not appreciably poisonous, should be avoided. Furthermore, as it is recognized or determined, in its various analytical reactions, only by its decomposition, to permit it to escape undecomposed, is so far to fail in the object of its production. The evolved gas should be constantly run into silver nitrate solution, or kept burning.

375. Arsenious hydride is decomposed by **heat** alone. In passing through glass tubes, heated to incipient redness, the gas is decomposed, the arsenic adhering to the inner surface of the tube, beyond the heated part, as a steel gray *mirror coating*. This coating is readily driven by the heat, is gradually dissipated by hot hydrogen gas, and imparts the garlic odor to the escaping hydrogen gas. The latter, if ignited, will generally deposit arsenic spots on porcelain, showing that the arsenic is not wholly retained in the tube.

376. Both the *mirror* and the *spots* exhibit the properties of free arsenic (365). Liquid reagents are most convenient for application to the spots. The reactions of these deposits having analytical interest are such as distinguish arsenic from antimony. Further, see the comparison of these elements with others of the Nitrogen Series, 584.

Comparison of Arsenic and Antimony, deposited from AsH_3 and SbH_3.

Arsenic Spots.	Antimony Spots.
Of a steel-gray to black *lustre.*	Of a velvety brown to black surface.
Volatile at 356° C.; as arsenious acid, at 218° C.	Volatile in vacuo at white heat; by oxidation, at a red heat.
Dissolve in *hypochlorite* (*a*).	Do not dissolve in hypochlorite.
Warmed with a drop of *ammonium sulphide*, form yellow spots (368), soluble in *ammonium carbonate*, insoluble in *hydrochloric acid.*	Warmed with ammonium sulphide, form orange-yellow spots, insoluble in ammonium carbonate, soluble in hydrochloric acid.
With a drop of hot nitric acid, dissolve clear (365).	With a drop of hot dilute nitric acid, turn white.
The clear solution, with a drop of solution of *silver nitrate*, when treated with vapor of ammonia (from a glass rod moistened with ammonium hydrate and held near), gives a brick-red or a yellow color (391).	The white fleck, treated with silver nitrate and vapor of ammonia, gives no color until warmed with a drop of ammonium hydrate, then gives a black color.
With vapor of *iodine*, color yellow, by formation of arsenious iodide, readily volatile when heated.	With vapor of iodine, color more or less carmine red, by formation of antimonious iodide, not readily volatile by heat.
Arsenic Mirror.	**Antimony Mirror.**
Deposited *beyond* the flame; the gas being decomposed by a red heat (375).	Deposited *before*, or on both sides of the flame; the gas being decomposed considerably below a red heat (411).
The mirror is *driven* at 356° C.; it does not melt.	The mirror melts to minute globules at 450° C., and then is driven at a red heat.
By vaporization in the stream of gas, escapes with a garlic *odor.*	The vapor has no odor.

By slow vaporization in a current of air (the tube open at both ends and held inclined over the heat), a deposit of octahedral *crystals* is obtained above—if abundant, forming a white coating (366), soluble in water, the solution giving reactions for arsenic.

By vaporization in a current of air, a white amorphous coating is obtained—insoluble in water, soluble in hydrochloric acid, and giving reactions for antimony.

a. The **hypochlorite** reagent—usually **NaClO**—decomposes in the air and light, by keeping. It should instantly and perfectly bleach litmus-paper (not redden it). It dissolves arsenic by oxidation, to arsenic acid:

$$2As + 5NaClO + 3H_2O = 2H_3AsO_4 + 5NaCl$$

377. When arsenious hydride is passed into solution of **silver nitrate**, the silver is reduced to metal (340) by the oxidation of both elements in the gas—the hydrogen to water, and the arsenic to arsenious acid, which remains in solution along with the liberated nitric acid (distinction from antimonious hydride, which precipitates silver antimonide, 411):

$$AsH_3 + 6AgNO_3 + 3H_2O = 6Ag + H_3AsO_3 + 6HNO_3$$

The *reactions for the arsenious oxide* formed in solution, should be obtained after filtering out the brown-black precipitate of silver, then adding a very little hydrochloric acid, that the silver in the undecomposed nitrate may be removed as chloride. From the filtrate, hydrosulphuric acid precipitates the sulphide, and arsenic may be quantitatively determined from the weight of this precipitate, after Marsh's Test. Reliance should not be placed on blackening of the silver nitrate alone; as this may be due to SbH_3, or to H_2S or to PH_3. H_2S would be generated in the test, from sulphides; and PH_3, from hypophosphites or phosphites.

If the material treated with zinc and dilute sulphuric acid be placed in a flask or large test-tube, and a paper moistened with silver nitrate be tied over the mouth, it will (on standing), be blackened by arsenious hydride. The interference of hydrosulphuric acid may be avoided by causing the gas to pass through cotton wool, moistened with solution of lead acetate, and carefully placed to fill the neck of the vessel, then left several hours. This operation may be relied on for negative results, in testing the purity of reagents, etc.

The yellow *silver arsenite* (370) may be obtained as a distinctive test, with the silver nitrate left in solution, undecomposed by the arsenious hydride, after filtering out only the metallic silver, by the careful addition of ammonium hydrate, in repeated small portions, by the glass rod, till the nitric acid and arsenious anhydride are just neutralized:

$$H_3AsO_3 + 3AgNO_3 + 6HNO_3 + 9NH_4OH = Ag_3AsO_3 + 9NH_4NO_3 + 9H_2O$$

Arsenious hydride received in **nitric acid** is changed to H_3AsO_4, soluble in water (separation from antimony).

378. Stannous chloride, $SnCl_2$, reduces arsenious and arsenic oxides, from hot concentrated hydrochloric acid solution, as flocculent, black-brown, metalloidal *arsenic*, con-

taining three or four per cent. of tin (Bettendorf's Method). The arsenic, in solution with the concentrated hydrochloric acid, *acts* as arsenious chloride (366 *b*):

$$2AsCl_3 + 3SnCl_2 = 2As + 3SnCl_4$$

The hydrochloric acid should be 25 to 33 per cent.; if not over 15 to 20 per cent., the reaction is slow and imperfect. Sulphuric acid with sodium chloride may be taken instead of hydrochloric acid:

In a wide test-tube, place 0.1 to 0.2 gram. (2 or 3 grains) of the (oxidized) solid or solution to be tested, add about 1 gram. (15 grains) of *sodium chloride*, and 2 or 3 cub. centim. (about one fluid drachm) of *sulphuric acid*, then about 1 gram. (15 grains) of crystallized *stannous chloride;* agitate, and heat to boiling several times, and set aside for a few minutes. Traces of arsenic give only a brown color; notable proportions give the flocculent precipitate. A dark-gray precipitate may be due to mercury (362, *a*), capable of being gathered into globules. If a precipitate or a darkening occurs, obtain conclusive evidence whether it contains arsenic or not, as follows: Dilute the mixture with ten to fifteen volumes of about 12 per cent. hydrochloric acid (equal parts of Fresenius's Reagent and water); set aside, decant; gather the precipitate in a wet filter, wash it with a mixture of hydrochloric acid and *alcohol;* then with alcohol, then with a little ether, and dry in a warm place. A portion of this dry precipitate is now dropped into a small hard-glass tube, drawn out and closed at one end, and heated in the flame: arsenic is identified by its mirror (375), easily distinguished from mercury (363). Antimony is not reduced by stannous chloride; other reducible metals give no mirror in the reduction-tube. Small proportions of organic material impair the delicacy of this reaction, but do not prevent it. It is especially applicable to the hydrochloric acid distillate, obtained in separation of arsenic, according to 384.

379. Metallic **copper** reduces arsenious oxide, from hydrochloric acid solution, as an iron-gray film or crust of *arsenic with copper*, 32 per cent. arsenic, or Cu_5As_2 (Reinsch's Method). The copper should be in bright strips, the solution hot, and the reaction awaited for some time. If much arsenic is present, the crust peels off in black scales. The crusts are not evidence of arsenic without further examination—according to 382, etc.—as antimony, silver, and other metals are reducible by copper. The film may be obtained and afterwards determined as arsenic, when but the 0.0005 gram. is taken in pure hydrochloric acid solution.

380. In Marsh's Test, a portion of the arsenic, reduced by the **zinc** to the elemental state, remains for a short time, while the arsenic is in excess in the solution, as a grayish-black film upon the zinc. If the generation of hydrogen be continued after the arsenic is all reduced, all the latter soon forms arsenious hydride. The deposition of antimony, in Marsh's Test, is much greater than that of arsenic. Also, if the operation be conducted in a platinum vessel or with platinum foil, in contact with the zinc, the reduced arsenic does not adhere to the platinum as firmly as the reduced antimony (408).

381. Potassium cyanide, with sodium carbonate, reduces arsenic from all its compounds, in the dry way:

$$As_2O_3 + 3KCy = 2As + 3KCyO$$

$$As_2S_3 + 3KCy = 2As + 3KCyS$$

$$As_2S_3 + 3Na_2CO_3 + 3KCy = 2As + 3Na_2S + 3KCyO + 3CO_2$$

If this reduction be performed in a small reduction-tube with a bulb at the end, the reduced arsenic sublimes and condenses as a mirror (376) in the cool part of the tube. The presence of compounds of manganese, bismuth, zinc, or antimony, hinders this reaction, but does not prevent it. The test can be performed in presence of mercury compounds, but more conveniently after their removal; in presence of organic material, it is altogether unreliable. If much free *sulphur* is present, H. Rose recommends that the arsenic should be removed from it, by dissolving in ammonia, evaporating the solution to dryness, oxidizing to arsenic acid with hydrochloric acid and potassium chlorate (385), precipitating with ammonium hydrate and magnesium solution as arseniate (388): and washing and drying the latter for the test.

The thoroughly dried substance is mixed with six times its bulk of a dry mixture of equal parts of anhydrous sodium carbonate and potassium cyanide, and introduced into the bulb of the reduction-tube, which should not be over half filled. Heat the bulb very gently over the flame, and if water rises and condenses in the tube, thoroughly dry the bulb and tube—wiping the inside of the tube with twisted paper. Then heat strongly, while the tube is held inclined, finally to a full red heat. If arsenic is present, the *mirror* will be seen above the bulb, and can be tested, as stated in 376, etc.

This operation becomes a more delicate test, and excludes antimony from the mirror, if the mixture be placed in a larger horizontal reduction-tube, drawn out narrow at one end, and connected at the other with an apparatus for generating and drying carbonic anhydride, which is passed over the substance during the reduction (Method of Fresenius and Babo):

Three parts of anhydrous sodium carbonate, with one of potassium cyanide, are taken, and ten or twelve parts of this mixture, to one part of the substance tested, the whole well mixed and thoroughly dried (in the water-oven). The reduction-tube should be about 1.25 centimeters (one-half inch) wide and 10 to 15 centimeters (four to six inches) long, besides the drawn out part. At the end not drawn out, it is connected with a small wash bottle, for sulphuric acid, and this connected with the flask for generating carbonic anhydride with marble and dilute hydrochloric acid. The dried mixture is introduced into the middle of the reduction-tube, by aid of a paper gutter; the connections made, and the substance again dried by gentle heat. When the atmosphere is expelled and a steady stream of carbonic anhydride is passing through the apparatus, heat the tube between the mixture and the drawn out end to redness, and then heat the mixture gradually to redness of the tube, driving the mirror to the narrowed portion of the tube. Finally, detach the tube, close the small end in the flame, and advance the heat up to the mirror.

382. Charcoal reduces arsenious oxide very readily, by heat in the glass tube. A small hard-glass tube is drawn out at one end, the extremity closed in the flame, and a particle of the well-dried material dropped into the tube, so that it will fall to the end of the narrow part. A fragment of recently burned charcoal is pushed down nearly to the substance, and heat applied, first to the charcoal and then to the substance, to redness. The mirror forms just above the heated part, and may farther be tested as stated in 376. During the reduction, the garlic *odor* is observed.

All compounds of arsenic, heated with sodium carbonate on charcoal, and all oxidized compounds heated on charcoal alone, present the odor of arsenic.

Non-oxidized forms of arsenic, heated in air, as in a **glass tube** open at both ends, oxidize to arsenious anhydride (365); and the latter substance sublimes in the tube, producing a *white coating* of microscopic octahedral crystals.

383. If dry arsenious anhydride is heated with dried **sodium acetate**, in the bulb of a small reduction-tube, *arsen-dimethyl oxide*, or cacodyl oxide, $As_2(CH_3)_4O$, is produced and recognized by its intensely offensive odor:

$$As_2O_3 + 4KC_2H_3O_2 = As_2(CH_3)_4O + 2K_2CO_3 + 2CO_2$$

384. Arsenic is removed from mixture with metallic salts and non-volatile acids, and obtained in a concentrated form, by **distilling** the mixture with concentrated hydrochloric acid—or sodium chloride and sulphuric acid—when *arsenious chloride* passes over at 132° C. (270° F.), and condenses with hydrochloric acid. (Regarding arsenic acid, see 395.) A flask over a sand-bath, with a tube passing through the stopper and then inclined downwards to a small receiving flask set in a vessel of cold water, constitutes a sufficient apparatus. The distillate may be examined according to 378.

385. Arsenious compounds are **oxidized** to arsenic compounds by a large number of oxidizing agents. As already stated (365 and 368 *e*, *f*), the solvents of elemental arsenic, and of arsenious sulphide, produce pentad arsenic compounds. Among the oxidations of arsenious compounds most used in analysis, are those by action of chlorine or bromine (*a*), iodine (*b*), nitric acid (*c*), copper sulphate with free fixed alkali (*d*), and permanganates (*e*). For other oxidations, see 843.

a. $H_3AsO_3 + 2Cl + H_2O = H_3AsO_4 + 2HCl$

b. $H_3AsO_3 + 2I + H_2O = H_3AsO_4 + 2HI$

c. $3H_3AsO_3 + 2HNO_3 = 3H_3AsO_4 + 2NO + H_2O$

d. $K_3AsO_3 + 2Cu(OH)_2 = K_3AsO_4 + Cu_2(OH)_2 + H_2O$

e. $5H_3AsO_3 + 2KMnO_4 + 6HCl = 5H_3AsO_4 + 2MnCl_2 + 2KCl + 3H_2O$

386. ARSENIC oxide, or anhydride, As_2O_5, is a white amorphous solid, melting at incipient red heat, and at full red heat vaporizing by decomposition into the volatile arsenious oxide and oxygen.—It is not directly **soluble** in water, but in contact with water it gradually forms its hydrates, the arsenic **acids**—tribasic, H_3AsO_4 or $3H_2O.As_2O_5$; dibasic, $H_4As_2O_7$ or $2H_2O.As_2O_5$; and monobasic, $HAsO_3$ or $H_2O.As_2O_5$—all of which are freely soluble in water, and soluble in alcohol; the solutions reddening litmus, and decomposing carbonates with effervescence. Arsenic anhydride slowly deliquesces in air, by formation of hydrates.—The monobasic and dibasic hydrates in contact with water gradually form tribasic hydrate; in fact, as acids, none of them are (like the phosphoric acids) definite and stable salts of hydrogen; but they represent three definite and stable series of metallic arseniates, which closely correspond in composition and in properties with the three classes of metallic phosphates (705). Of these, the tribasic arseniates—represented by H_3AsO_4—have the greatest importance. They are trimetallic, as K_3AsO_4; di-metallic, as K_2HAsO_4; and mono-metallic, as KH_2AsO_4.

The *arseniates* of the alkali metals are all **soluble** in water; only the mono-metallic arseniates of the other metals are soluble in water, but their di- and tri-metallic arseniates are soluble in arsenic acid (as mono-metallic salts) and in the stronger mineral acids (by decomposition). In acetic acid, they dissolve with more or less difficulty; many of them are soluble in solutions of ammonium salts.

In **analysis**, the formation of arsenious hydride occurs alike with pentad and triad arsenic (397). For distinctions from arsenious compounds, see 398.

387. Hydrosulphuric acid precipitates, very tardily, in solutions of arsenic acid or acidulated arseniates, the yellow *arsenious sulphide*, with free

sulphur, $As_2S_3 + S_2$. In the cold, addition of solution of hydrosulphuric acid causes no appreciable immediate effect (distinction from arsenious acid); but, by treatment with the gas for 12 to 24 hours, better at about 70° C. (160° F.), all the arsenic can be thrown down. Also, more readily, by previous reduction, according to 394. The precipitate has the properties stated in 366 and 368, with the additional properties of free sulphur, which in its recent condition is taken up by alkali hydrates.

Ammonium sulphide precipitates solutions of arsenic acid, more rapidly than is done by hydrosulphuric acid, as *arsenic sulphide*, As_2S_5—readily soluble in excess of the reagent, as ammonium sulpharseniate, $(NH_4)_3AsS_4$.

Thiosulphates react as with arsenious compounds (369), free sulphur being separated.

When the precipitate of $As_2S_3 + S_2$ is dissolved by alkali sulphides, sulpharsen*iates* are formed, as K_3AsS_4 or $3K_2S.As_2S_5$, and $K_4As_2S_7$ or $2K_2S.As_2S_5$, variably tribasic and dibasic. Thus:

$$As_2S_3.S_2 + 2(NH_4)_2S = 2(NH_4)_2S.As_2S_5 \quad [= (NH_4)_4As_2S_7]$$

Dilute ammonium hydrate, and ammonium carbonate, however, dissolve the arsenious sulphide as sulpharsen*ite* and arsenite (366 *d*), leaving the free sulphur undissolved.

388. **Magnesium salts** with ammonium chloride, and free ammonium hydrate precipitate *ammonium-magnesium arseniate*, $MgNH_4AsO_4$, white, easily soluble in acids (distinction from arsenites). The reagents should be first mixed together, and used in a clear solution—"the magnesium mixture"—to make sure that enough ammonium salt is present to prevent the precipitation of magnesium hydrate, by the ammonium hydrate. The precipitate forms slowly and with crystallization, but completely. Compare with the corresponding ammonium magnesium phosphate (117).

389. Solution of **barium hydrate** precipitates solution of arsenic acid partially, and solution of alkali arseniates almost completely, as *barium arseniate*, $BaHAsO_4$, from dimetallic solutions, and $Ba_3(AsO_4)_2$ from monometallic. The precipitate is sparingly soluble in water. If **ammonium hydrate** is added with the baryta, the *ammonium-barium arseniate*, $BaNH_4AsO_4$, is precipitated, insoluble in water, and not made soluble by ammonium salts or by ammonium hydrate (distinction from arsenites).

The tri- and di-metallic *calcium* arseniates are insoluble in water; the ammonium calcium arseniate, $CaNH_4AsO_4$, is sparingly soluble.

390. Salts of the **third and second group metals** precipitate solutions of arsenic acid but slightly, but precipitate solutions of tri-metallic and di-metallic alkali arseniates completely (as, respectively, tri-metallic and di-metallic arseniates)—in accordance with the solubilities of arseniates stated in 386.

391. **Silver nitrate** solution precipitates neutralized arsenic acid as *silver arseniate*, Ag_3AsO_4, reddish-brown; the solubilities and conditions of precipitation being the same as for the arsenite (370).

Copper sulphate solution precipitates solutions of arseniates as *copper arseniate*,

$CuHAsO_4$, greenish-blue, the solubilities and conditions of precipitation being the same as for the arsenites (371).

392. Ferric salts, with alkali acetates, precipitate, from solution of arsenic acid, or from acidulated solution of arseniates, *ferric arseniate*, $Fe_2(AsO_4)_2$, yellowish-white, insoluble in acetic acid (compare equation in 188). Ferric salts alone precipitate, from dimetallic arseniates, two-thirds metallic ferric arseniate, $Fe_2H_3(AsO_4)_3$.

393. Ammonium Molybdate $(NH_4)_2MoO_4$, in nitric acid solution, gives a yellow precipitate of *ammonium arsenio molybdate*, of variable composition. Compare Phosphomolybdates (494).

394. Reducing agents change arsen*ic* compounds either into arsen*ious* compounds only, or into elemental arsenic. **Sulphurous acid** and sulphites (*a*), **thiosulphates** (*b*), **hypophosphites** (*c*), **oxalic acid** (*d*), **stannous salts** (*e*), and **ferrous** salts in concentrated hydrochloric acid solution at 132° C. (*f*), reduce arsenic acid to arsenious acid without farther change; also, the precipitation of arsenic acid as arsenious sulphide involves reduction by **hydrosulphuric acid**—a reduction precisely corresponding to that of ferric salts in their precipitation as ferrous sulphide. For the study of reductions of pentad arsenic, see 844.

a. $H_3AsO_4 + H_2SO_3 = H_3AsO_3 + H_2SO_4$

b. $H_3AsO_4 + Na_2S_2O_3 = H_3AsO_3 + Na_2SO_4 + S$

c. $2H_3AsO_4 + NaH_2PO_2 = 2H_3AsO_3 + NaH_2PO_4$

d. $H_3AsO_4 + H_2C_2O_4 = H_3AsO_3 + H_2O + 2CO_2$

e. $H_3AsO_4 + SnCl_2 + 2HCl = H_3AsO_3 + SnCl_4 + H_2O$

f. $H_3AsO_4 + 2FeCl_2 + 5HCl = Fe_2Cl_6 + 4H_2O + AsCl_3$

395. By reaction *f*, of the preceding paragraph, we are enabled to remove the arsenic in arsen*ic* acid, from mixture of non-volatile inorganic salts and acids, by **distillation** of *arsenious chloride*—as directed for arsen*ious* acid, in paragraph 384. In presence of water, neither heat with hydrochloric acid alone, nor ferrous salts without heat, convert arsenic acid to arsenious chloride. The hydrochloric acid should be as strong as 25 per cent.; otherwise, sodium chloride and concentrated sulphuric acid should be used instead.

396. Arsenic acid vaporizes by decomposition at a low red heat (as stated in 386); but, in absence of reducing agents, the arseniates of the alkali metals bear **full ignition** without change. In the removal of organic matter by combustion, excess of potassium nitrate must be added to counteract the reducing influence of the carbon. After fusion as sodium arseniate, antimony is separated by insolubility, according to the plan in 463.

397. The **reducing agents** which separate metalloidal arsenic *from arsenious compounds*, effect the same result with arsenic acid, though not quite so readily. The analytical methods described in 373 to 383, inclusive, have all been given for arsenious and arsenic oxides alike. In solution of arsenic acid in water, *without other acid*, **zinc** and other metals do not effect reduction, but are dissolved as acid arseniates with evolution of hydrogen:

$$Zn + 2H_3AsO_4 = ZnH_4(AsO_4)_2 + 2H$$

398. The reactions *distinguishing between arsenious and arsenic acids* have been described: action of arsenious acid as a reducing agent, 385; the precipitation of ammonium earth-metal arseniates, 388; of arsenio molybdate,

393; the slow precipitation of arsenic acid by hydrosulphuric acid, 387; the colors of the silver salts, 370 and 391, and of the copper salts, 371 and 391.

ANTIMONY.

399. A lustrous, bluish-white, brittle, and readily pulverizable **metal**, fusible at 425° C. (797° F.), and slowly volatile at a white heat.—It is but little tarnished in dry air; in moist air it **oxidizes** slightly, with formation of a blackish-gray mixture of metal and antimonious oxide; when melted, it oxidizes quickly, and at a red heat it burns with a white light, and white, inodorous vapors—the formation of the antimonious oxide, Sb_2O_3. —Boiling concentrated hydrochloric acid slowly **dissolves** powdered antimony (*a*), but when in the compact state it resists that acid; boiling concentrated sulphuric acid slowly converts it into antimonious sulphate with evolution of sulphurous anhydride (*b*); nitric acid rapidly oxidizes it, the dilute acid forming chiefly antimonious oxide (*c*), the concentrated forming mostly Sb_2O_4 and antimonic anhydride (*d*)—these oxides being insoluble in the dilute, slightly soluble in the concentrated acid; nitro-hydrochloric acid rapidly converts the metal into soluble antimonious chloride and insoluble oxides (*e*); but if the nitric acid be added to the hydrochloric acid in very small portions during the solution, only the antimonious chloride is formed (*f*). Boiling solution of tartaric acid slowly dissolves precipitated antimony (*g*). Alkalies do not dissolve it.

a. $Sb + 3HCl = SbCl_3 + 3H$

b. $2Sb + 6H_2SO_4 = Sb_2(SO_4)_3 + 6H_2O + 3SO_2$

c. $2Sb + 2HNO_3 = Sb_2O_3 + H_2O + 2NO$

d. $6Sb + 10HNO_3 = 3Sb_2O_5 + 5H_2O + 10NO$ (460)

and $3Sb + 4HNO_3 = 3SbO_2 + 2H_2O + 4NO$

e. $Sb + 3Cl = 3SbCl_3$, then, with a part of this solution:

$2SbCl_3 + 3H_2O = Sb_2O_3 + 6HCl$

also: $2Sb + 10Cl + 5H_2O = Sb_2O_5 + 10HCl$

f. $Sb + Cl_3 = SbCl_3$

g. $2Sb + H_2(C_4H_4O_6) + 2H_2O = (SbO)_2(C_4H_4O_6) + 6H$

400. Antimony forms two typical **oxides**, each having corresponding salts; antimonious oxide, Sb'''_2O_3, representing the metal as a feeble base; and antimonic anhydride, $Sb^v_2O_5$, which does not form a stable acid, but unites with bases, though with less electro-negative power than the corresponding compound of arsenic.

401. ANTIMONIOUS *oxide* is slightly soluble in water, insoluble in alcohol; freely soluble, by full or partial combination, in aqueous solutions of tartaric (*a*), hydrochloric (*b*), and other acids, not in nitric acid; soluble in strong solutions of alkalies. The *chloride* is very deliquescent, and freely soluble in water acidulated with hydrochloric acid or with tartaric or citric acid, soluble in aqueous solution of sodium chloride and soluble in alcohol.

The *bromide* requires tolerably concentrated hydrobromic, and the *iodide*, quite concentrated hydriodic acid, for solution. The *sulphates* require moderately concentrated sulphuric acid for solution (compare 261; and see, further, 402). The *tartrate* is soluble in water without acidulation; the potassium antimonious tartrate, soluble in water, and in glycerine, insoluble in alcohol.

a. $Sb_2O_3 + H_2(C_4H_4O_6) = (SbO)_2(C_4H_4O_6) + H_2O$

b. $Sb_2O_3 + (6+n)HCl = 2SbCl_3 + 3H_2O + nHCl$

In **analysis**, antimony sulphide is separated, with arsenic and tin sulphides, from other second group precipitates, by solution in ammonium sulphide (455). The separation from arsenic and tin is effected through antimonious hydride (409 and 411).

402. Water decomposes the acidulated solutions of antimonious salts, with precipitation of a portion as *basic salt*, and the separation of acid, which, restoring the acid strength lost by dilution with the water, holds the other portion of the original salt in solution. In solution of the chloride, $SbCl_3$, the basic salt precipitated by water is the white antimonious *oxychloride*, **SbOCl**, "Powder of Algaroth":

$$SbCl_3 + H_2O = SbOCl + 2HCl$$

The composition of the precipitate is variable, however, each addition of water removing more hydrochloric acid, and leaving the precipitate nearer to the normal oxide. For example:

$$3SbCl_3 + 4H_2O = Sb_3O_4Cl + 8HCl$$

The precipitate is soluble in tartaric acid (distinction from bismuth, 288). In presence of sufficient tartaric or citric acid, water does not decompose antimonious chloride; the *tartrates* of antimony, and of antimony and potassium, being dissolved by water without decomposition. The water solution of tartrate is liable to precipitation of basic salt by *hydrochloric*, sulphuric, and nitric acids.

403. Solutions of the **fixed alkali hydrates** precipitate, from the acidulated solution of antimonious chloride or of other inorganic antimonious salt, in absence of tartaric and citric acids, the white and bulky *antimonious oxide*, Sb_2O_3, quite readily soluble in excess of the reagents, more quickly by heating; soluble in solution of fixed alkali carbonates when heated, but scarcely at all in the cold; insoluble in ammonium hydrate. The precipitate is slightly soluble in water, and becomes crystalline after warming, if no alkali hydrate is present. It dissolves readily in solution of tartaric acid (401 *a*), also in that of potassium hydrogen tartrate (*a*).

The solution of antimonious oxide by alkalies is due to its combination with them, acting as a feebly acidulous anhydride and forming *antimonites*, which are found to be

monobasic, so far as capable of isolation (*b*). Sodium antimonite, $NaSbO_2$, is the most stable and least soluble in water: potassium antimonite, $KSbO_2$, is freely soluble in dilute potassium hydrate solution, but decomposed by pure water. By **long standing** (24 hours), a portion of the antimonious oxide deposits from the alkaline solution, and the presence of alkali hydrogen carbonates causes a nearly complete separation of that oxide (equation *c*, 404):

$$a.\quad Sb_2O_3 + 2KH(C_4H_4O_6) = 2KSbO(C_4H_4O_6) + H_2O$$

$$b.\quad 2SbCl_3 + 6KOH = Sb_2O_3 + 6KCl + 3H_2O$$

$$Sb_2O_3 + 2KOH = 2KSbO_2 + H_2O$$

$$\text{Or:}\quad SbCl_3 + 4KOH = KSbO_2 + 3KCl + 2H_2O$$

Ammonium hydrate gives the same precipitate, Sb_2O_3, scarcely at all soluble in excess.

404. The alkali **carbonates** likewise precipitate *antimonious oxide* (*a*) soluble in a strong excess of the fixed alkali carbonates when warmed (*b*) (distinction from tin); insoluble in excess of ammonium carbonate (distinction from antimonic oxide). The solution in fixed alkali carbonates deposits antimonious oxide on cooling and standing (*c*):

$$a.\quad 2SbCl_3 + 3K_2CO_3 = Sb_2O_3 + 6KCl + 3CO_2$$

$$b.\quad SbCl_3 + 4K_2CO_3 + 2H_2O = KSbO_2 + 3KCl + 4KHCO_3$$

$$c.\quad 2KSbO_2 + 2KHCO_3 = Sb_2O_3 + 2K_2CO_3 + H_2O$$

405. **Hydrosulphuric acid** precipitates, from not too strongly acidulated solutions of antimonious salts, the orange-red *antimonious sulphide*, Sb_2S_3 (hydrated), slightly soluble in pure water, insoluble in water containing H_2S. In neutral solutions (tartrate) the precipitation is imperfect, non-acidulated solution of the potassio tartrate being only colored; in strong hydrochloric acid solutions and in strong alkaline solutions, the precipitation is prevented. Alkali **sulphides** give the same precipitate, soluble in excess of the reagents (*a*), then reproduced by acids as antimonic sulphide (*b*). The *antimonious sulphide is soluble* in fixed **alkalies** (*c*); in **alkali sulphides**, more readily if they contain excess of sulphur (*a*) and quite difficultly in normal (colorless) ammonium sulphide; only slightly soluble in ammonium hydrate and scarcely at all soluble in **ammonium carbonate** (distinction and separation from arsenic, 368); slowly soluble by boiling solution of fixed alkali carbonate (*d*) (distinction from tin); soluble in **hydrochloric acid**, either moderately dilute or stronger (separation from arsenic, 368) (*e*); soluble in nitro-hydrochloric acid (*f*); insoluble in solutions of acid sulphites (distinction from arsenic, 461); left insoluble by **nitric acid** (separation from arsenic, 460).

In the solutions in **alkali sulphides**, the antimonious sulphide exists as alkali **sulphosalt**; sulphantimoniate when from action of yellow ammonium sulphide (equation *a*):

a. $Sb_2S_3 + 3(NH_4)_2S_2 = 2(NH_4)_3SbS_4 + S$

b. $2(NH_4)_3SbS_4 + 6HCl = Sb_2S_5 + 6NH_4Cl + 3H_2S$

c. $Sb_2S_3 + 4NaOH = Na_3SbS_3 + NaSbO_2 + 2H_2O$

d. $Sb_2S_3 + 2Na_2CO_3 = Na_3SbS_3 + NaSbO_2 + 2CO_2$

e. $Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$

f. $Sb_2S_3 + 6Cl = 2SbCl_3 + 3S$ (dissolving as H_2SO_4)

or $Sb_2S_3 + 10Cl + 5H_2O = Sb_2O_5 + 10HCl + 3S$

406. **Thiosulphates**—as $Na_2S_2O_3$—likewise precipitate *antimonious sulphide* (separation of arsenic and antimony from tin, 462):

$$2SbCl_3 + 3Na_2S_2O_3 + 3H_2O = Sb_2S_3 + 3Na_2SO_4 + 6HCl$$

407. **Potassium cyanide** gives a white precipitate.—**Ferrocyanides** (in absence of tartaric acid) give a white precipitate, insoluble in acids.—**Oxalic acid** (in absence of tartaric acid) gives a white crystalline precipitate, forming slowly but completely. **Potassium iodide** with hydrochloric acid in antimonious solutions gives only a yellow color—no free iodine (*distinction from antimonic acid, see* 423).

408. Antimonious oxide is **reduced to the elemental state** by agents, and with reactions, similar to those effecting the reduction of arsenious oxide.

Stannous chloride, however, does not reduce it (distinction from arsenic).

The **metals**: magnesium, zinc, iron, cadmium, lead, tin, copper, and bismuth, precipitate from antimonious solutions (in absence of nitric acid) the brown-black *metallic antimony*:

$$2SbCl_3 + 3Zn = 2Sb + 3ZnCl_2$$

If antimony be reduced from a dilute hydrochloric acid solution by **zinc, on platinum** foil or in a platinum dish, the larger portion of the antimony is deposited as a brown or black *adherent coating* or stain on the platinum, while a portion passes off as antimonious hydride along with free hydrogen. The stain is removed by warm nitric, not by hydrochloric acid. In this test, tin deposits as a loose, spongy mass, soluble in hydrochloric acid (434), and arsenic does not closely adhere to the platinum (380).

409. If **hydrogen** be generated, more abundantly than in the operation last mentioned, by zinc with dilute sulphuric or hydrochloric acid, in a Marsh's apparatus, a smaller portion of antimony is deposited with the zinc, while *antimonious hydride*, SbH_3, is obtained for examination (compare arsenic, 373):

$$Sb_2O_3 + 6Zn + 6H_2SO_4 = 6ZnSO_4 + 3H_2O + 2SbH_3$$

$$SbCl_3 + 3Zn + 3HCl = 3ZnCl_2 + SbH_3$$

410. *Antimonious hydride* **burns** with a luminous and faintly bluish-green flame, dissipating vapors of antimonious oxide and of water (*a*); or depositing antimony on **cold porcelain** held in the flame, as a lustreless brownish-black ***spot*** (*b*). The gas is also decomposed by passing through a small glass tube

heated to low redness, forming a lustrous ring or *mirror* in the tube. The spots and mirror of antimony are compared with those of arsenic in 376.

a. $2SbH_3 + 6O = Sb_2O_3 + 3H_2O$

b. $2SbH_3 + 3O = 2Sb + 3H_2O$

411. When the *antimonious hydride* is passed into a solution of **silver nitrate**, the silver is reduced by the hydrogen, leaving all the antimony with the silver, as silver antimonide, Ag_3Sb, a black precipitate (distinction from arsenic, which enters into solution, 377):

$$SbH_3 + 3AgNO_3 = Ag_3Sb + 3HNO_3$$

If the precipitate be removed and washed free from undecomposed silver salt (and arsenious acid, if that be present), the antimony may be dissolved out by boiling *for some time with concentrated* solution of tartaric acid (399 *g*). Also, **hydrochloric acid**, more readily, dissolves the antimony from Ag_3Sb, though it cannot dissolve uncombined antimony. The solution consists of antimonious chloride, leaving **AgCl**. The solution may be tested for antimony by hydrosulphuric acid. Also, SbH_3 received in **nitric acid** changes to Sb_2O_5, insoluble in water (separation from **As**).

412. All compounds of antimony are completely **reduced in the dry way** on charcoal with sodium carbonate, more rapidly with potassium cyanide; the metal fusing to a brittle globule (compare 399). The reduced metal rapidly oxidizes, the white oxide rising in fumes, and making a crystalline deposit on the support. The same white oxide is formed on heating antimony or its sulphides in a **glass tube** (*b*). The equations for reduction correspond to those given for arsenic, in 381.

413. The **oxidation** of antimonious compounds to antimonic compounds requires strong oxidizing agents; that is, antimonious oxide is not a powerful reducing agent. A list of its oxidations is given in 841. The action of nitric acid and chlorine has been stated in connection with metallic antimony (399 *d* and *e*). Silver oxide (414), gold chloride (415), chromic acid (416), and permanganates, oxidize antimonious compounds, their reactions (especially the first-named), giving us delicate **tests in distinction from antimonic compounds.** For distinction of antimonic compounds, see, also, the oxidizing action of antimonic acid on iodides in 423.

414. Solution of **silver nitrate**—with the **potassium** or sodium hydrate solution of antimonious oxide, $KSbO_2$—gives a black precipitate of *argentous oxide*, Ag_4O (see equation), insoluble in **ammonium hydrate**, and mixed with gray argentic oxide, which is dissolved out by the ammonia. If chlorides are present in the solution, the silver chloride produced will also dissolve in ammonium hydrate, leaving only the black argentous oxide. Now, the alkaline antimoni*ates*, formed if antimonic compound was present in the substance taken in this test, precipitate white silver antimoniate, *soluble in ammonium hydrate* (leaving still the evidence of antimonious compounds):

$$KSbO_3 + 2Ag_2O \text{ (see 330)} = Ag_4O + KSbO_3$$

Silver nitrate, in acid solution of antimonious chloride, precipitates Sb_2O_3 with **AgCl**, the latter dissolving in **ammonium hydrate**, and leaving the former (no oxidation of the antimony being effected):

$$2SbCl_3 + 6AgNO_3 + 3H_2O = Sb_2O_3 + 6AgCl + 6HNO_3$$

In solution of potassium antimonious *tartrate*, silver nitrate precipitates only silver tartrate, soluble in ammonium hydrate, the antimonious oxide being held in solution as a tartrate. Thus:

$$2KSbO(C_4H_4O_6) + 2AgNO_3 = Ag_2(C_4H_4O_6) + (SbO)_2(C_4H_4O_6) + 2KNO_3$$

415. Solution of **auric chloride**, $AuCl_3$ is reduced, in boiling (acid) solution of antimonious chloride, to metallic *gold*, as a yellow precipitate, mixed with **antimonic oxide** as a larger bulk of white precipitate, unless much excess of hydrochloric acid is present to hold antimonic chloride in solution (420):

$$4AuCl_3 + 3Sb_2O_3 + 6H_2O = 4Au + 3Sb_2O_5 + 12HCl$$

416. Chromic acid—obtained with $K_2Cr_2O_7 + 2HCl$—is reduced to *chromic salt*, Cr_2Cl_6, by acid antimonious solutions; the liquid turning green, and *antimonic oxide*, Sb_2O_5, being precipitated or left in solution—as a sparing or abundant excess of acid is present (420).

417. ANTIMONIC oxide, or *anhydride* (see 400), is a yellowish powder, but slightly **soluble** in water; soluble in concentrated hydrochloric acid and in tartaric acid, scarcely at all in nitric acid. Antimonic *chloride*, $SbCl_5$, is completely decomposed by water; the *sulphide*, Sb_2S_5, insoluble in water.

There are two hydrogen antimoniates or **acids**: *antimonic acid*, $H_2OSb_2O_5$ or $HSbO_3$, monobasic; and *metantimonic acid* $(H_2O)_2Sb_2O_5$ or $H_4Sb_2O_7$, dibasic, or isomeric with antimonic acid and monobasic; the former being produced when antimony is dissolved by excess of nitric acid (399 *d*), or when an antimoniate is decomposed by a stronger acid (420); the latter being formed in the decomposition of antimonic chloride by water. Free metantimonic acid holds $(H_2O)_2$ in addition to the basic water.

418. *Antimonic acid* (ordinary modification), $HSbO_3$, is sparingly **soluble** in water, reddens litmus, and dissolves in concentrated hydrochloric acid, or, slowly, in a large proportion of water acidulated with that acid; also in tartaric acid. It dissolves, by combination, with cold solution of potassium hydrate, but not in cold solution of ammonium hydrate. By fusion with potassium hydrate it is changed to a salt of metantimonic acid. —*Metantimonic acid*, dibasic $H_4Sb_2O_7$ or $(H_2O)_2Sb_2O_5$, and monobasic $HSbO_3$, is more soluble in water, in acids, and in ammonium hydrate, than antimonic acid, its isomer, into which it easily changes.

The *normal antimoniates*—as $KSbO_3$—are all **insoluble** in water, except a hydrated potassium antimoniate, and this is made anhydrous and insoluble by boiling in solution. The *super-antimoniates*, as $K_2O(Sb_2O_5)_2$, are all insoluble in water. The *dibasic metantimoniates*—as $(K_2O)_2Sb_2O_5$—are insoluble in water, but the potassium and the ammonium salts dissolve intact in water containing much alkali hydrate. All dibasic metantimoniates are decomposed by pure water with formation of *monobasic metantimoniates*—as $K_2OSb_2O_5$ or $KSbO_3$—isomeric with the normal antimoniates. Of the monobasic metantimoniates, only those of potassium and ammonium are soluble in water.

419. The monobasic potassium metantimoniate, or "granular antimoniate of potassium," $KSbO_3$, is used as a **precipitant for sodium** (48), and is prepared by fusing anti-

monic acid with large excess of potassium hydrate; then dissolving, filtering, evaporating, and digesting hot, in syrupy solution, with large excess of potassium hydrate, best in a silver dish, decanting the alkaline liquor, and stirring the residue to granulate, dry. This reagent must be kept dry, and dissolved when required for use; inasmuch as, in solution, it changes to the dibasic metantimoniate, which does not precipitate sodium. The reagent is, of course, not applicable in acid solutions.

420. Slight additions of **water** precipitate the concentrated hydrochloric acid solutions of antimonic acid, or antimonic chloride, as dibasic *metantimonic acid*, $(H_2O)_2Sb_2O_5$ or $H_4Sb_2O_7$ (417); the precipitate being sparingly soluble in the acidulated liquid.—**Acids** precipitate, from solutions of alkali antimoniates and metantimoniates, the corresponding antimonic *acid*, $HSbO_3$ or $H_4Sb_2O_7$. Tartaric acid prevents these precipitations.

421. **Hydrosulphuric acid** and sulphides precipitate the orange-colored *antimonic sulphide*, Sb_2S_5, having the solubilities stated for antimonious sulphide, in 405—antimon*ic* compounds forming in the solution. Both dibasic and tribasic sulphantimoniates are formed. The typical, tribasic salts occur as follows:

$$Sb_2S_5 + 3(NH_4)_2S_2 = 2(NH_4)_3SbS_4 + 3S \quad \text{(Compare 405, } a.\text{)}$$

$$Sb_2S_5 + 6HCl = 2SbCl_3 + 2S + 3H_2S \quad (\text{“ } 405, e.)$$

$$Sb_2S_5 + 6Cl = 2SbCl_3 + 5S \quad (\text{“ } 399, e.)$$

$$\text{Or: } Sb_2S_5 + 10Cl + 5H_2O = Sb_2O_5 + 10HCl + 5S$$

422. Antimonic acid is **reduced** to metal by all the reducing agents stated for antimonious oxide in 408, having the same behavior with zinc and platinum, and in Marsh's test:

$$Sb_2O_5 + 8(Zn + H_2SO_4) = 8ZnSO_4 + 5H_2O + 2SbH_3$$

Stannous chloride reduces antimonic to antimonious compounds, but, as stated in 408, does not reduce the latter:

$$SbCl_5 + SnCl_2 = SbCl_3 + SnCl_4$$

423. Antimonic acid is reduced to *antimonious iodide* by hydriodic acid, as follows (distinction from antimonious compounds, 407):

$$SbCl_5 + 5KI = SbI_3 + 2I + 5KCl$$

If **potassium iodide** is added to hydrochloric acid solution of antimonic compounds, a dark brown precipitate of iodine appears; if only antimonious compound is present, the solution is colored yellow, but remains clear. In both cases, free hydriodic acid is formed. If the proportion of antimonic compound be very slight, the liberated iodine will still be revealed by its violet color in the subsiding layer, after agitation with carbon disulphide and subsidence. Of course, the liquid and the hydrochloric acid must be strictly free from uncombined chlorine, and the iodide must contain no iodate—that is, the two reagents must not precipitate each other.

424. By **ignition**, in the absence of reducing agents, antimonic acid and

anhydride are reduced to antimonious antimoniate, $Sb_2O_3Sb_2O_5$; or SbO_2, antimony dioxide; otherwise given as Sb_2O_4; a compound unchanged at a red heat, and obtained for quantitative determinations.

425. The antimoniates of the fixed alkali metals are not vaporized or decomposed when **ignited** in absence of reducing agents. Hence, by **fusion** in the crucible with soda and oxidizing agents—*i.e.*, with **sodium nitrate and carbonate**—the compounds of antimony, and of arsenic (396), are converted into non-volatile sodium metantimoniate and arseniate, $Na_4Sb_2O_7$, and Na_3AsO_4. If now the fused mass be digested and disintegrated in cold water and filtered, *the* **antimoniate** *is separated as a residue* ($NaSbO_3$—418), *while the* **arseniate** *remains in solution* with the excess of alkali. The operation is much more satisfactory when the arsenic and antimony are previously fully oxidized—as by digestion with nitric acid—as the oxidation by fusion in the crucible is not effected soon enough to retain all of the arsenic or antimony which may be in the state of lower oxides, sulphides, etc. If compounds of **tin** are present in this operation—and if the fusion is not done with excess of heat, so as to convert sodium nitrite to caustic soda and form the soluble sodium stannate—the tin will be left as stannic oxide, SnO_2, in the residue with the $NaSbO_3$. But if sodium hydrate is added in the operation, the tin is separated as stannate in solution with the arsenic. For a plan of separations, based on these facts, see 463.

TIN.

426. A lustrous white **metal**, fusible at 230° C. (446° F.), volatile (when not in contact with the air) at a white heat.—It **tarnishes** a very little in pure air or with moisture, but more in air containing hydrosulphuric acid; when fused in the air it forms a mixture of stannous and stannic oxides with moderate rapidity; at a white heat it burns in the air with a dazzling white light, and formation of stannic oxide; at a red heat it decomposes steam with evolution of hydrogen.—It **dissolves** with hydrochloric acid, slowly when the acid is dilute and cold, but rapidly when hot and concentrated—stannous chloride and hydrogen being produced (*a*); in dilute sulphuric acid, slowly, with separation of hydrogen (*b*); in hot concentrated sulphuric acid, rapidly, with separation of sulphurous anhydride and sulphur (*c*); nitric acid concentrated does not act upon it, the dilute acid rapidly converts it into metastannic acid, insoluble in acids (*d*); very dilute nitric acid dissolves it without evolution of gas as stannous nitrate and ammonium nitrate (*e*); nitrohydrochloric acid dissolves tin easily as stannic chloride (*f*); potassium hydrate solution dissolves it very slowly, and by atmospheric oxidation (*g*); or, at high temperatures, with evolution of hydrogen (*h*).

a. $Sn + 2HCl = SnCl_2 + 2H$

b. $Sn + H_2SO_4 = SnSO_4 + 2H$

c. $Sn + 2H_2SO_4 = SnSO_4 + 2H_2O + SO_2$, and then

$2SnSO_4 + SO_2 + 2H_2SO_4 = 2Sn(SO_4)_2 + S + 2H_2O$

d. $3Sn + 4HNO_3 = 3SnO_2 + 2H_2O + 4NO$ (compare 438)

e. $4Sn + 10HNO_3 = 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3$

f. $Sn + 4Cl = SnCl_4$

$$g.\quad Sn + 2KOH + O = K_2SnO_2 + H_2O$$

$$h.\quad Sn + 2KOH = K_2SnO_2 + 2H$$

427. Tin forms two stable oxides and corresponding **classes of salts** : stannous oxide, $Sn''O$, and stannic oxide, $Sn''''O_2$; the latter acts both as a base, in stannic compounds, and as an acidulous anhydride, in stannates of metals. Stannous compounds readily change to stannic compounds by contact with the air and by nearly all oxidizing agents (437), being themselves powerful reducing agents; stannic compounds are not easily reduced to stannous combinations, being feeble oxidizing agents. In respect to the relative stability of its two classes of salts, tin resembles iron; stannous salts, however, are relatively less permanent than ferrous salts—in accordance with the fact that stannic sulphide is formed, and ferric sulphide is not formed, in precipitation by sulphides.

428. STANNOUS oxide, hydrate, sulphide, oxy-chloride, phosphate, and oxalate, are **insoluble** in water. The chloride requires quite strongly, and the nitrate moderately acidulated water for solution; the bromide, the iodide, and sulphate, dissolve in pure water (261).

Tin is **separated**, as a sulphide, with arsenic and antimony, from other second group sulphides, by solution with yellow ammonium sulphide (455): from arsenic and antimony it is easily separated by reduction in Marsh's test (435). Stannous salts are distinguished by their reducing power (437).

429. Water partially decomposes the acidulated solution of stannous chloride; precipitating *stannous oxychloride*, soluble in acids, the liberated acid preventing complete precipitation:

$$2SnCl_2 + H_2O = Sn_2OCl_2 + 2HCl$$

The **atmosphere** causes, in solutions of stannous chloride, a precipitate of *stannous oxychloride* with formation of *stannic* chloride; a change which occurs in the reagent kept in bottles frequently opened, and is retarded by presence of sufficient hydrochloric acid with metallic tin.

$$3SnCl_2 + O = Sn_2OCl_2 + SnCl_4$$

430. The **alkali hydrates** precipitate, from solutions of stannous salts, *stannous hydrate*, $Sn(OH)_2$, white, readily soluble in excess of the fixed alkali hydrates, as alkali stannite, K_2SnO_2, insoluble in ammonium hydrate (distinction from antimony):

$$SnCl_2 + 2KOH = Sn(OH)_2 + 2KCl$$

$$Sn(OH)_2 + 2KOH = K_2SnO_2 + 2H_2O$$

By boiling, the precipitate becomes anhydrous, **SnO**, without change of color. Boiling in strong potassium hydrate solution, more quickly by the addition of a little tartaric acid, blackens the precipitate, which now contains metallic tin.

Alkali **carbonates** also precipitate *stannous hydrate*, insoluble in excess (distinction from antimony). Barium carbonate precipitates all the tin as hydrate, in the cold.

431. **Hydrosulphuric acid** and sulphides precipitate the dark-brown *stannous sulphide*, **SnS** (*a*), hydrated, insoluble in dilute, soluble in moderately dilute acids, as stated below. Thiosulphates do not give a precipitate —distinction from arsenic (369), and from antimony (406).

Stannous sulphide is readily dissolved by alkali supersulphides, the yellow sulphides, with formation of *sulphostannates* (*b*), from which acids precipitate the yellow *stannic sulphide* (442) (*c*), but the normal, colorless, alkali sulphides scarcely dissolve any stannous sulphide. **Potassium hydrate** and **sodium hydrate** dissolve it as *stannites* with *sulphostannites* (*d*), from which acids precipitate again the brown *stannous sulphide* (*e*); ammonium hydrate and the alkali carbonates do not dissolve it (distinction from arsenic, 368, and with fixed carbonates distinction from antimony, 405 *d*). It is not soluble by acid sulphites (distinction from arsenic, 368).—**Hydrochloric acid** dissolves it, as *stannous chloride*, with evolution of hydrosulphuric acid (*f*); nitro-hydrochloric acid—free **chlorine**—as *stannic chloride* with residual sulphur (*g*); nitric acid oxidizes it to metastannic acid, without solution (separation from arsenic, 460).

a. $SnCl_2 + H_2S = SnS + 2HCl$

b. $SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3$

c. $(NH_4)_2SnS_3 + 2HCl = SnS_2 + 2NH_4Cl + H_2S$

d. $2SnS + 4KOH = K_2SnO_2 + K_2SnS_2 + 2H_2O$

e. $(K_2SnO_2 + K_2SnS_2) + 4HCl = 2SnS + 4KCl + 2H_2O$

f. $SnS + 2HCl = SnCl_2 + H_2S$ (for SnS_2, see 442).

g. $SnS + 4Cl = SnCl_4 + S$

432. **Potassium iodide** precipitates—from solutions not very dilute, as nearly neutral as possible and free from stannic salt—the yellow *stannous iodide*, SnI_2, sparingly soluble in water, more soluble in warm than cold water, and slightly decomposed by water with precipitation of variable, yellow, stannous oxy-iodides ; slightly soluble in excess of the reagent, the potassio stannous iodide being mostly decomposed by water, less in dilute solutions; soluble in hydrochloric acid, and in solution of potassium hydrate. With **stannic salts** in water solution, the iodides react as follows (see 439):

$$SnCl_4 + 4KI = SnI_4 + 4KCl$$

And, simultaneously: $SnI_4 + 3H_2O = SnO(OH)_2 + 4HI$

433. Alkaline **phosphates** precipitate *stannous phosphate*, $Sn_3(PO_4)_2$, white, variable by conditions.—**Oxalates** precipitate *stannous oxalate*, SnC_2O_4, white.—**Ferrocyanides** give a white gelatinous precipitate; **ferricyanides**, a white precipitate (with stannic salts, no precipitate).—**Cyanides** precipitate *stannous hydrate*, with liberation of hydrocyanic acid.

434. Tin is **reduced** by **zinc**: from freely acidulated stannous or stannic solutions, as a gray *spongy mass* (**Sn**); from alkaline solutions, as lustrous crystals. With **zinc on platinum** foil or in a platinum dish, the tin reduced, from acid solutions, collects mostly on the zinc, does not stain or adhere to the platinum, and, however reduced, *dissolves in hydrochloric acid* (426 *a*) (dis-

tinctions from antimony and from arsenic; see 408). But reduction by metallic **aluminium**, or **magnesium**, is much more prompt and satisfactory.

435. In Marsh's Test for arsenic (373) and antimony (409), if tin is present, it will be deposited as a dark-colored powder, as stated in the preceding paragraph, not adherent to the zinc. Arsenic is deposited early in the operation, and finally all removed in the gas; antimony is not wholly, but is mostly removed, at the last; tin, not at all. If all the zinc is permitted to dissolve while the acid is not expended, the deposit of tin will slowly dissolve in the dilute acid. Indeed, tin may be used instead of zinc, in Marsh's Test. With zinc present, the tin does not dissolve; and after the arsenic has all been expelled in the gas, *the tin may be rinsed away from the zinc by the water-jet, and dissolved with moderately concentrated hydrochloric acid*, while any antimony present remains undissolved (426 *a*, and 399 *a*). The antimony may afterwards be quickly dissolved by nitro-hydrochloric acid, and tested.

436. Before the **blow-pipe**, on **charcoal**, with sodium carbonate, and more readily by addition of potassium cyanide, tin is reduced to malleable lustrous globules—brought to view (if minute, under a magnifier) by repeated trituration of the mass with water, and decantation of the lighter particles. A little of the white incrustation of stannic oxide will collect on the charcoal near the mass, and by persistence of the flame on the globules, the same coating forms upon them. This coating, or oxide of tin, moistened with solution of **cobalt nitrate**, and again ignited strongly, becomes of a blue-green color.

437. Stannous salts are **oxidized to Stannic Salts** by a large number of reagents (see 427). Stannous chloride is one of the most convenient and efficient of the ordinary, discriminative deoxidizing agents, for operations in the wet way. As stannic chloride is soluble in the solvents of stannous chloride, no precipitate of tin is made by its reducing action; but many other metals are so precipitated by reduction to insoluble forms. Thus:

Mercuric chloride is reduced from solution, first to white *mercurous* chloride, and then to gray *mercury* (362 *a*); **silver** nitrate, to brown-black silver (340); **arsenic**, from arsenic to arsenious compounds (394 *e*), and all soluble compounds, to black precipitate of *arsenic* (378); **antimonic** compounds, to soluble antimonious compounds (422); bismuth salts, to monoxide (297); **chromic acid**, to green *chromic* salt, left in solution (166 *f*); **ferric** salts, to *ferrous* salts, left in solution (171 *d*); **auric** chloride, to the violet precipitate of *gold* (475). **Sulphurous anhydride**, in ordinary relations a strong reducing agent, serves to oxidize stannous chloride; warm digestion with sulphites and hydrochloric acid giving a precipitate of *stannic oxy-sulphide*, $(SnO_2)_5SnS_2$. Nitric acid changes stannous to stannic compounds, chiefly with formation of *nitric oxide* and *ammonium nitrate*.—**Ferricyanides** effect the same change, with formation of *ferrocyanides;* and **permanganates**, with production of *manganous salts*. Many of these reactions are applicable in **distinguishing stannous from stannic salts**. A very dilute mixture of ferricyanide and ferric salt makes a delicate, though not distinctive test for tin as a dyad.

438. STANNIC oxide or anhydride (see 427) forms two well-marked hydrates or **acids**: *stannic acid*, H_2SnO_3, and *metastannic acid*, $H_{10}Sn_5O_{15}$ (variable). Stannic acid

is formed by precipitating stannic salts with alkalies (440); metastannic acid, by action of nitric acid on tin (426 *d*, then—$5SnO_2 + 5H_2O = H_{10}Sn_5O_{15}$).

Stannic acid is **insoluble** in water, but readily forms soluble stannic salts with hydrochloric, sulphuric, and nitric acids, and soluble alkali stannates with the alkali hydrates; other stannates being insoluble. *Metastannic acid* is insoluble in acids, and does not form metastannic salts; but dissolves in fixed alkalies, with formation of metastannates.

439. The *stannic* oxide, hydrate, sulphide, and phosphate, are **insoluble** in water. The chloride and bromide are scarcely at all decomposed by water; the iodide, almost wholly decomposed by water (see equation, 432). The relations of stann*ous* chloride, bromide, and iodide, to water, are each quite the reverse of the corresponding stannic haloids, as shown by comparison with 428. Stannic sulphate is decomposed by boiling its water solution. Stannic chloride and iodide are soluble in alcohol.

440. The **alkali hydrates** and **carbonates**, and barium carbonate, precipitate from solutions of stannic salts, *stannic acid*, H_2SnO_3, white; soluble in excess of fixed alkali hydrates and carbonates; insoluble in ammonium hydrate and carbonate (distinction from antimony). The alkaline solutions contain stannates:

$$SnCl_4 + 4KOH = H_2SnO_3 + 4KCl + H_2O$$
$$H_2SnO_3 + 2KOH = K_2SnO_3 + 2H_2O$$
$$SnCl_4 + 2(NH_4)_2CO_3 + H_2O = H_2SnO_3 + 4NH_4Cl + 2CO_2$$
$$H_2SnO_3 + K_2CO_3 = K_2SnO_3 + H_2O + CO_2$$

441. A peculiar precipitation of *metastannic acid*, $H_{10}Sn_5O_{15}$, is produced by most normal alkali salts, on boiling in concentrated solution. Thus:

$$5SnCl_4 + 20Na_2SO_4 + 15H_2O = H_{10}Sn_5O_{15} + 20NaCl + 20NaHSO_4$$
$$5SnCl_4 + 20NH_4NO_3 + 15H_2O = H_{10}Sn_5O_{15} + 20NH_4Cl + 20HNO_3$$

442. **Hydrosulphuric acid** and sulphides precipitate *stannic sulphide*, SnS_2, hydrated, yellow, having the solubilities given in 431 for stann*ous* sulphide, with this difference, that stannic sulphide is moderately soluble in **normal**, colorless, **alkali sulphides**. With the stannic sulphide precipitate, yellow, we have these reactions, *different from those in* 431; the others being the same as with stannous sulphide:

$SnCl_4 + 2H_2S = SnS_2 + 4HCl$ Corresponding to 431, *a*.

$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3$ " " " *b*.

$SnS_2 + (NH_4)_2S_2 = (NH_4)_2SnS_3 + S$

$2SnS_2 + 4KOH = K_2SnO_3 + K_2SnS_3$
$+ H_2S + H_2O$ " " " *d*.

$(K_2SnO_3 + K_2SnS_3 + H_2S) + 4HCl =$
$2SnS_2 + 4KCl + 3H_2O$ " " " *e*.

$SnS_2 + 4HCl = SnCl_4 + 2H_2S$ " " " *f*.

443. **Phosphates** precipitate basic *stannic phosphate,* $Sn_2O(PO_4)_2$, white; **Ferrocyanides** give a white, and **ferricyanides**, no precipitate.

444. Stannic salts are **reduced** *to Stannous* **Salts** by metallic **tin** or **copper.**

$$SnCl_4 + Sn = 2SnCl_2$$

Concerning the reduction of stannic compounds to metal, see 434, and **blow-pipe reactions**, 436.

The behavior of stannic oxide in fusion with sodium hydrate and carbonate —used in separation from antimony and from arsenic—is described in 425 and in 463.

445. Comparison of Certain Reactions of Arsenic, Antimony, and Tin.

Taken as Arsenious Oxide, Antimonious Chloride, Stannous Chloride, or other soluble Compounds.

	As‴	Sb‴	Sn″
H_2S forms colored sulphides, soluble in $(NH_4)_2S_2$, and in alkalies, reprecipitated by acids.	As_2S_3, yellow, insoluble in **HCl**, soluble in $(NH_4)_2CO_3$ (368).	Sb_2S_3, orange, soluble in **HCl**, insoluble in $(NH_4)_2CO_3$ (405).	**SnS**; brown (SnS_2 yellow), soluble in **HCl**, insoluble in $(NH_4)_2CO_3$ (431).
NH_4OH **in excess.**	No precipitate.	Sb_2O_3, white (403).	$Sn(OH)_2$, white (430).
Zn and dilute H_2SO_4	AsH_3 (gas) (373). In $AgNO_3$, forms **Ag** and H_3AsO_3 (377).	SbH_3 (gas) (409). In $AgNO_3$ forms Ag_3Sb, black precip. (411).	**Sn**, a gray mass (435).
Dilution of saturated solutions.	. . . . .	**SbOCl**, white. Dissolved by tartrate (402).	Sn_2OCl_2, white (429).
HNO_3, concentrated, acting on the solids.	H_3AsO_4 (385). Gives certain of the reactions of H_3PO_4 (388).	Sb_2O_4 and Sb_2O_5, insoluble (399 *d*, and 413).	SnO_2, insoluble (426 *d*, and 437).

SEPARATION OF THE METALS OF THE FIRST AND SECOND GROUPS.

446. The separation of the **First Group metals**—lead, silver, and mercury of mercurous salts—**from the other bases of the Second Group,** *by hydrochloric acid,* is complete for silver and mercury, but incomplete for lead (313). Lead could be separated from other second group metals *by sulphuric acid* in *dilute* solution; but this applied to the original solution would also precipitate the fourth group metals, and requires a different grouping of the bases, as by Zettnow's process (472). So it is identified, if abundant, in the first group, and then removed in the second group (after the separation by ammonium sulphide) *by sulphuric acid.* In removing lead as a sulphide, if hydrochloric acid is present, the solution should be quite dilute (313).

447. Although the only insoluble metallic chlorides are the plumbic, argentic, and mercurous, yet *hydrochloric acid may produce precipitates in certain solutions which contain no first group base.* The following are some of the conditions in which this occurs:

a. An acid solution of antimony, bismuth, or tin, with some other acid than hydrochloric, and saturated with water, as far as possible without precipitation, on the addition of hydrochloric acid, precipitates *the oxychloride* of the metal in question (288, 402, 429). These precipitates are readily soluble in excess of the hydrochloric acid, but so is a very slight precipitate of silver chloride (328).

b. In a saturated solution of certain salts, as barium chloride, hydrochloric acid precipitates the salt *without chemical change;* the precipitate soluble in a small proportion of water (84).

c. In solutions of higher sulphides, as Na_2S_2 (368, *c*), and of thiosulphates, as $Na_2S_2O_3$ (697)—these solutions having an alkaline reaction—hydrochloric acid forms a precipitate of *sulphur* (700).

d. The solutions containing *double sulphides* of alkali metals and arsenic, antimony, tin (gold, platinum, molybdenum, iridium); *double iodides* of bismuth, copper, and first group metals; *double cyanides* of class (1) 617, and certain *double thiosulphates,* are liable to precipitation in the first group, as represented in equation *b,* 617. All these precipitates, except those of first group metals, are soluble in excess of the hydrochloric acid.

e. All the alkaline solutions of metallic oxides, as potassium zinc oxide, are precipitated at the neutral point in the addition of acids.

f. Alkaline solutions of antimonic, silicic, boracic (tungstic, molybdic, tantalic, and niobic) acids; also of benzoic, salicylic, uric, and certain other organic acids, are precipitated by acidulation with mineral acids, many of the precipitates being soluble in hydrochloric acid. (Thallious salts are precipitated as chloride.)

g. Acidulation with hydrochloric acid may induce changes of oxidation or reduction, which, in certain mixtures, result in precipitation.

If the solution taken for the grouping of the bases has an alkaline reaction, it cannot contain a normal salt of a first group base; it may contain a basic lead salt, or one of the compounds noticed in *c, d, e,* or *f.*

If the first group precipitate be more than very slightly dissolved by farther addition of water or of hydrochloric acid, it should be so dissolved before proceeding with the analysis. If the precipitate is colored, or if it is found not to accord with the reactions of any of the first group bases, it should be treated separately, as a solid substance taken for examination.

448. The separation of the **First Group bases from each other**, according to the **Table**, 794, is exceedingly simple. $PbCl_2$ is dissolved in abundance of *hot water;* **AgCl**, in *ammonium hydrate;* while Hg_2Cl_2 is left insoluble in a characteristic black form, as NH_2HgCl.

If the lead chloride is not all washed out with hot water, the ammonium hydrate will change it to insoluble basic salt (309), and leave it with the mercury on the filter.

Let it be observed, if the first group precipitate contains but one base, the action of ammonium hydrate determines which it is: lead chloride does not change color; silver chloride dissolves; mercurous chloride blackens.

449. The presence of **lead** is easily ascertained in the dilute solution of its chloride. A portion of this solution is treated for the sulphate, according to the **Table** (794); carefully avoiding excess of acid (312); an illustration of the important *relations of lead salts with sulphates.* Other portions of this dilute solution give the more delicate test with hydrosulphuric acid, and the characteristic test with chromates, and serve to illustrate the important relations with carbonates and phosphates; but a more concentrated solution must be used in studying the precipitates which are soluble in excess of their precipitants—those by fixed alkali hydrates, iodides, bromides, etc. (Concerning lead in second group relations, see 467.) Among the other tests made in study of first and second group metals, those involving reduction by metals and other agents should never be neglected.

450. The presence of **silver**, in its ammoniacal first group solution, is determined according to the Table by reprecipitation with nitric acid, as **AgCl**. This test is exceedingly delicate, provided too much alkali chloride is not formed in the solution (328). For small quantities, it is better to expel the excess of ammonium hydrate by heat before adding the nitric acid, which must not be in excess.

For farther illustrative tests, reduce the chloride to metallic silver (340), either by zinc, set aside in the test-tube, or by stannous salts, or sugar with alkali; then wash the reduced silver thoroughly, and dissolve it in nitric acid, as $AgNO_3$.

451. The remaining base, **mercury**, as the black mercurosammonium chloride, for the farther tests in the wet way, may be obtained as soluble mercuric salt by solution in nitro-hydrochloric acid. Good evidence of the mercurous combination of the mercury has been obtained in the first group precipitation, and in the color of the product with ammonium hydrate; but if the original solution is found not to contain other interfering metals, it may after-

wards be used to obtain the distinctive reactions of mercurous salts with iodides, chromates, phosphates, etc.

452. In the **precipitation of the Second Group,** the *acidulation* requires attention. It must not be omitted because of an acid reaction of the original solution, unless it is known that free mineral acid is present. It must be sufficient for the formation of arsenious sulphide (368), and not too strong for complete precipitation of antimonious sulphide (405 *e*). If the original solution is strongly acid—as after solution of dry substances by mineral acids—the excess of acid must be reduced by evaporation. Free chlorine is incompatible with the group precipitant, and if present must be fully expelled.

453. Precipitates may occur in the second group, when no second group metal is present. The precipitations by mere acidulation have been excluded by the first group work, but the precipitation of free sulphur may occur, as follows: (*a*) with fading of a previous brownish-yellow tint, from ferric salts (186); (*b*) appearing with a green color, deeper than a previously existing red or yellow color, or from nearly colorless solutions, due to chromic acid (166 *a*); (*c*) from free chlorine, bromine, or iodine, liberated by the dilute acid of the group reagents acting with chlorates, nitrates, bromates, iodates, hypochlorites, etc., of the original substance. Indeed, several of these substances decompose hydrosulphuric acid without the aid of other acids.

All the bases precipitated in the second group are thrown down as *colored* sulphides—yellow, orange, brown, or black—readily distinguishable from sulphur by the lighter color and the lighter specific gravity of the latter. The precipitate of sulphur may be disregarded—except as an indication of the possible presence of some of the oxidizing agents, and, with the changes of color mentioned in (*a*) and (*b*), especially indicative that iron or chromium will be found in the next group.

454. It will be remembered that **pentad arsenic** is not precipitated short of treatment with the hydrosulphuric acid gas for several hours (387). Unless this time can be taken, the arsenic must be reduced to arsenious acid—by sulphurous acid (394 *a*), or otherwise—or the systematic course of analysis may be departed from. In the latter case, the original solution may be used in Marsh's Test, if it do not contain nitrates or other oxidizing agents; or the reduction in the dry way (381) may be employed.

455. The **separation of the bases of the Second Group,** according to the **Table,** 795, begins with a division into three classes, by action of two solvents, yellow ammonium sulphide, and moderately concentrated nitric acid. We have, *in the precipitated sulphides:*

(1) **As, Sb, Sn**—dissolved as sulphosalts by $(NH_4)_2S_2$.

(2) **Pb, Cu, Bi, Cd**—dissolved as nitrates by HNO_3.

(3) **Hg**—dissolved as chloride by **Cl.**

456. Before applying **ammonium sulphide,** the precipitate of sulphides must be washed clean of acid, and of all substances in the filtrate. Whether the digestion is performed on the filter, or in the test-tube or beaker, the amount of solvent should be as small as possible.

The insoluble portion is filtered out, washed first with a little sulphide of ammonium, then with several portions of hot water, and set aside.

It is first to be determined whether any base has been dissolved by the sulphide of ammonium. This may be done, in a small portion, by a drop of dilute acid; if the precipitate be white, uncolored, either no sulphides of **As, Sb, Sn,** were in the group precipitate, or they were in small proportion, and overwhelmed by the solvent. We place here together the representative equations:

$$2(NH_4)_3AsS_3 + 3H_2SO_4 = As_2S_3 \text{ (yellow)} + 3(NH_4)_2SO_4 + 3H_2S$$

$$2(NH_4)_3SbS_4 + 3H_2SO_4 = Sb_2S_5 \text{ (orange)} + 3(NH_4)_2SO_4 + 3H_2S$$

$$(NH_4)_2SnS_3 + H_2SO_4 = SnS_2 \text{ (yellow)} + (NH_4)_2SO_4 + H_2S$$

$$(NH_4)_2S_2 + H_2SO_4 = S \text{ (white)} + (NH_4)_2SO_4 + H_2S$$

It is evidently easy to mask the color of the sulphides by an excessive proportion of free sulphur, some of which will always be present; and, in case of any doubt, perhaps, as a general practice, it is better to proceed with the ammonium sulphide solution, to the final tests for arsenic, antimony, and tin.

457. There is this imperfection in the separation of **As, Sb,** and **Sn,** as sulphides, by ammonium sulphide; that **copper** as sulphide is slightly dissolved by the same solvent (276). Acids reprecipitate the copper sulphide, generally as normal **CuS,** but sometimes as a liver-colored super-sulphide, which, with excess of sulphur, has nearly the color of SnS_2, or As_2S_3. The amount of copper so dissolved and reprecipitated is small, and cannot simulate notable quantities of arsenic, antimony, or tin; but such a small loss of copper from the nitric acid solution of the group lessens the delicacy of the work for that metal. Therefore, it is especially important to *identify copper in the preliminary examination*—by the bead or on charcoal, if the substance is solid, and by the tint, if in solution, and by the reduction on a strip of clean iron (280).

Now, the *fixed alkali super-sulphides*—Na_2S_2 or K_2S_2—do not dissolve copper sulphide in the least, and they serve as solvents of the sulphides of **As, Sb,** and **Sn,** as well as ammonium sulphide; but they dissolve mercuric sulphide (359 *b*), to an extent that involves a greater imperfection in the separations of the group, than does the use of ammonium sulphide. However, if the preliminary examination shows mercury to be absent, it is better to use fixed alkali sulphide for the separation of copper from arsenic, antimony, and tin.

458. Having removed the bases soluble as ammonium sulphosalts from the rest of the group, we have to separate **arsenic, antimony, and tin, from**

each other. This may be accomplished in several ways by certain solvents, acting on the *sulphides.* And, to this end, the sulphides are reproduced; the whole remaining alkaline sulphidic solution (456) being reprecipitated by an acid. If we employ separative *solvents,* we may choose between three (368), viz.: *ammonium carbonate,* dissolving As_2S_3 and leaving the other sulphides; *hydrochloric acid,* leaving As_2S_3 undissolved and dissolving the other two sulphides (405 *e,* and 442, last equation); and *alkali sulphites,* which dissolve As_2S_3 and leave the antimony and tin undissolved. Neither one of these solvents effects a strict separation, and more exact and satisfactory results are obtained by Marsh's operation (373); receiving all the gas in solution of silver nitrate (411), and treating the residue in the generator for tin (435). This plan is the one given in the **Table** for the second group (795).

459. The separation of arsenic by ammonium carbonate, as a solvent, has been used in the following plan:

Sulphides Precipitated from the $(NH_4)_2S_2$ Solution: As_2S_3, Sb_2S_5, SnS_2, (S), (456).

Digest with Solution of Ammonium Carbonate and Filter (366 *d*).

Residue: SnS_2, Sb_2S_5, (S).

Dissolve in hot **hydrochloric acid** (442, 421).

Solution: $SnCl_4$, $SbCl_3$.

Treat with **zinc** *and* **hydrochloric acid** *in presence of Platinum foil, in Marsh's apparatus* (435).

Deposit: Sn, (Sb).

Dissolve by **hydrochloric acid.**

Solution: $SnCl_2$.

(Residue, **Sb**).

Test by mercuric chloride (362 *a*).

Examine by 445, *etc.*

Gas: SbH_3.

(Test the spots, 376.)

Receive the gas in solution of **silver nitrate.** *Dissolve the precipitate* (Ag_3Sb) (411), *and test by* H_2S.

Compare by 445.

Solution: $(NH_4)_3AsS_3 + (NH_4)_3AsO_3$

Precipitate by **hydrochloric acid;** *filter; wash the precipitate and dissolve it by* **chlorine** *generated from a minute fragment of potassium chlorate and a little hydrochloric acid* (368 *e*).

Expel all free chlorine (373).

Solution: H_3AsO_4.

Apply Marsh's Test, as directed in 373, *testing the spots* (376); *receiving the gas in solution of* **silver nitrate,** *and testing the resulting solution* (377).

Examine the original solution, as indicated in 445, *and the text.*

The plan above given may be varied by *separating antimony and tin by ammonium carbonate* in fully oxidized solution, as follows: The Sb_2S_5 and SnS_2 are dissolved by nitro-hydrochloric acid, to obtain the antimony as metantimonic acid. The solution is then treated with excess of *ammonium carbonate,* in a vessel wide enough to allow the carbonic acid to escape without waste of the solution. The $(H_2O)_2Sb_2O_5$, forms the

soluble ammonium metantimoniate, $2(NH_4)_2O.Sb_2O_5$ (dibasic), or $(NH_4)_2O.Sb_2O_5$ (monobasic).

Meanwhile the $SnCl_4$ is fully precipitated as SnH_2O_3 (equation in 440); and may be filtered out from the solution of metantimoniate.

The liability of failure, in this mode of separating antimony and tin, lies in the non-formation of metantimonic acid by nitro-hydrochloric acid. The ordinary antimonic acid forms a less soluble ammonium salt (418), but this acid is not so likely to occur in dissolving as *antimonious chloride*, $SbCl_3$ (according to 421). Now, excess of ammonium carbonate does not redissolve the Sb_2O_3 which it precipitates from $SbCl_3$, as stated in 404.

460. Separation of Arsenic from **Sb, Sn, Bi, Cu,** and **Hg,** by treatment of their sulphides with strong Nitric Acid—the resulting nitrates being decomposed by heat.* The washed precipitate of sulphide is treated, in an evaporating dish, with nitric acid of sp. grav. 1.2 or stronger, that which is brown by presence of nitrogen oxides being best, until brown vapors are no longer evolved. The mixture is then evaporated to dryness. If separation from copper or bismuth is desired, the heat must be slowly increased (by use of a sand bath) to a temperature of 400° to 600° C., not reaching a red heat, and in all cases insuring the expulsion of all sulphuric and nitric acids. The residue is now digested with hot water (for about ten minutes), and filtered. **Solution:** H_3AsO_4. **Residue:** Sb_2O_4 or Sb_2O_5, SnO_2, CuO and basic copper salt, Bi_2O_3, HgS. If copper and bismuth are to be separated, the heat must be sufficient to vaporize sulphuric acid, which is necessarily formed. For separation of arsenic from antimony and tin, this is a convenient method, and gives exact results. The residue of antimony is soluble in nitro-hydrochloric acid; that of tin, slowly soluble in hot hydrochloric acid.

461. The solubility of arsenic sulphide (368 *d*), and the insolubility of sulphides of antimony and tin in solution of *acid sodium sulphite*, furnish a basis for the following:

Plan for Separating Arsenic Sulphide by Acid-Sulphites, and Antimony and Tin Sulphides, by Nitric and Tartaric Acids.

After precipitation of the solution of sulphosalts with dilute *hydrochloric acid* and some hydrosulphuric acid, and washing:

Precipitate (*a*): As_2S_3, Sb_2S_5, SnS_2, (free sulphur).

Transfer *precipitate* (*a*) to a test-tube or beaker, and digest at the boiling point, for some time, in a solution of *sodium acid sulphite* with free sulphurous acid. Filter and wash the residue.

Solution (*b*): $Na_2O.As_2O_3$, $Na_2S_2O_3$; $(NaHSO_3)$ (368, *d*).

Residue (*c*): Sb_2S_5; SnS_2 (free sulphur).

Acidulate *solution* (*b*) with *hydrochloric acid*; add *hydrosulphuric acid*, and digest, warm; if a precipitate occurs, treat it in an evaporating dish with nitric acid; filter and wash from the excess of sulphur; concentrate the solution, and test it for **arsenic** by Bettendorf's method (378), or by reduction with cyanide (381).

* Victor C. Vaughan: *Amer. Chem.*, vi. (1875) 41; vii. (1877), March.

Digest *residue* (*c*) with hot, *concentrated nitric acid* in an evaporating dish, and expel the excess of acid.

Product (*d*): Sb_2O_4; SnO_2 (sulphur and H_2SO_4) (399 *d*, 426 *d*).

Treat the *product* (*d*) with hot solution of *tartaric acid*, and filter.

Solution (*e*): $(SbO)_2C_4H_4O_6$; (excess of acids).—(401 *a*.)

Residue (*f*): SnO_2, as metastannic acid (sulphur).

Test *solution* (*e*) with hydrosulphuric acid (and hydrochloric acid) for **antimony**; testing further by dissolving the sulphide, etc.

Fuse *residue* (*f*), with sodium carbonate and *cyanide*, on charcoal, and examine for tin (436). Dissolve in hydrochloric acid; test with mercuric chloride, etc.

462. If the *acid solution* of **As**, **Sb**, and **Sn**—prepared by dissolving the sulphides in hydrochloric acid with potassium chlorate—is treated with boiling **solution of sodium thiosulphate**, the arsenic and antimony are precipitated as sulphide (369 and 406), the tin left in solution.

The *sulphides* of **As** and **Sb**, so produced, may now be separated by hot solution of sulphites with sulphurous acid, as directed for precipitate *a*, 461; leaving the arsenic in solution, and the antimony as residue.

We now have:

Solution (*a*): $SnCl_4$. (Precipitate by H_2S; also reduce with **Zn** and test.)

Solution (*b*): $Na_2O.As_2O_3$. (Treat as directed for solution *b*, 461.)

Residue (*c*): Sb_2S_5. (Dissolve in hydrochloric acid, and test.)

463. The separation of **As**, **Sb**, and **Sn**, by fusion with sodium salts and oxidizing agents, is indicated in 425. It will be seen, from the statements at the close of that paragraph, that when SnO_2 is fused with sodium hydrate, a stannate of sodium (Na_2SnO_3) is formed, which dissolves in water; but when fused with sodium carbonate and nitrate (at a heat which does not convert the latter salt to caustic soda), it remains as stannic oxide, insoluble in water.

Now, the fusion of fully oxidized arsenic and antimony with sodium carbonate and nitrate (with or without caustic soda) converts both these elements into the (non-volatile) sodium arseniate and dibasic metantimoniate—Na_3AsO_4 and $Na_4Sb_2O_7$—the arseniate soluble, and the antimoniate insoluble, in cold water. The dibasic metantimoniate is insoluble in water by conversion into monobasic salt, $NaSbO_3$, if the water be not strongly alkaline (418).

Hence, fusion of fully oxidized **As**, **Sb**, and **Sn** with sodium hydrate, enables us to separate antimony from arsenic and tin; fusion, with sodium carbonate, etc., without sodium hydrate, separating arsenic from antimony and tin.

The fusion with sodium hydrate requires a silver crucible.

Separation of fully oxidized Arsenic, Antimony, and Tin, by fusion with Sodium Carbonate and Nitrate, and Reduction.

The sulphides precipitated by hydrochloric acid from the solution of sulphosalts are taken for oxidation.

Precipitate (*a*): As_2S_5; Sb_2S_5; SnS_2 (sulphur).

Digest, in an evaporating dish, with hot *nitric acid*, in repeated portions, and evaporate to dryness at a gentle heat.

Residue (*b*): As_2O_5; Sb_2O_5; SnO_2 (free sulphur).

Mix with one or two parts of *sodium carbonate*, and two or three parts of *sodium nitrate; fuse* (in a porcelain crucible), for some time, and until the mass is quiet, at a heat not much above the fusing point of the mass. Pour the fused mass upon a cold slab; pulverize, and digest in *cold water*. Filter.

Solution (*c*): Na_3AsO_4 (sodium carbonate and nitrite).

Residue (*d*): $Na_4Sb_2O_7$ and (by action of water) $NaSbO_3$; SnO_2.

Acidulate solution (*c*) with acetic acid and test it with magnesia mixture, etc., for **arsenic**, according to 388, etc. The various precipitated arseniates may be collected, and with the remaining portion of solution (*c*), submitted to Marsh's Test.

Treat residue (*d*) with *concentrated hydrochloric acid*, hot, until dissolved. *Dilute* until the solution is sparingly acidulated and transfer to a platinum dish, or a porcelain dish with a piece of *platinum* foil (rinsing out any white residue which may have been precipitated by the water), and proceed to *reduce* antimony and tin, *with zinc*, according to 408.

Deposit (*e*): **Sb** (staining the platinum); **Sn** (not adherent).

Rinse the dark, spongy precipitate from the zinc with water, and remove the zinc. Treat the precipitate and the stained platinum with hot, moderately concentrated hydrochloric acid. Treat the stained platinum separately, first with hot nitric acid, then with concentrated solution of tartaric acid.

Solution (*f*): $SnCl_2$; $ZnCl_2$. (Test for tin, with mercuric chloride.)

Solution (*g*): $(SbO)_2C_4H_4O_6$. (Obtain the sulphide; dissolve in solution of K_2CO_3.—405 *d*).

If with the fusion, as above, sodium hydrate be added:

Solution (*c*): Na_3AsO_4; Na_2SnO_3 (sodium hydrate, carbonate and nitrite).

Residue (*d*): $Na_4Sb_2O_7$ and (by action of water) $NaSbO_3$.

Acidulate solution (*c*) with *sulphuric acid*, and expel all nitrous gas, and conduct Marsh's Test for **arsenic**; examining the residue for **tin**, according to 435.

Dissolve residue (*d*) with hydrochloric acid; obtain the sulphide of **antimony**; dissolve the latter, and test.

464. The **Second Portion** of the second group bases—obtained as stated in 455, and washed as specified in 456—is dissolved in hot, moderately dilute *nitric acid*. Nitrous gas passes off, instead of hydrogen sulphide; and sulphur is left, together with the black mercuric sulphide, if any mercury is present. The solution occurs mostly with evolution of **NO**, and essentially as shown for copper, and lead, in equations 276 *a*, and 311 *a*. Traces of **HgS** may dissolve; and, if the nitric acid be strong and its action prolonged, more than traces of $PbSO_4$ (white) may be formed, and left insoluble with the mercury—according to equation *b*, 311. Some, or all, of the lead sulphate may be dissolved by the strong nitric acid; but, as the acid loses strength in the digestion and during filtration, it will precipitate from this solution. And it is even less soluble in *dilute* sulphuric acid, its precipitant, than in water (308).

The excess of nitric acid is mostly expelled by evaporation, and water is added, but not sufficient to precipitate bismuth (288); and if a white precipitate is seen to form on dilution, it is dissolved by sufficient nitric acid.

465. The solution is now tested, consecutively:

(*a*), with sulphuric acid (and alcohol) to precipitate lead;

(*b*), unless removed in first group, with hydrochloric acid to precipitate silver;

(*c*), with excess of ammonium hydrate to precipitate bismuth, white (289),
to dissolve copper, blue (274),
and to dissolve cadmium, colorless (301).

Tests (*a*) and (*b*) are each made in a small portion of the material; if, by test (*a*), lead is detected, then lead is removed from the whole material by precipitation with sulphuric acid and filtration. The same course is pursued with test (*b*); and in ordinary analysis silver is never found in this group, being removed in the first group. This precaution provides against the addition of a large excess of mineral acids to the whole material, which will then be so greatly diluted by neutralizing with ammonium hydrate that test (*c*) is of no value. And in case lead (and silver) have to be removed, the filtrate should be evaporated to expel the excess of acid, then used for test (*c*).

466. Some analysts dissolve the sulphides, (2) 455, in concentrated nitric acid, then dilute and add dilute sulphuric acid (and alcohol) *before* filtration; **leaving the lead with the mercury—$PbSO_4$** with **HgS**. This residue is then boiled with *ammonium acetate*, which dissolves the lead sulphate, as stated in 312, and leaves the black mercuric sulphide (with free sulphur) undissolved.

467. In any case, the addition of *alcohol* renders the sulphuric acid test for **lead** much more delicate (312); but the alcohol must be added very sparingly, and with a full knowledge that cupric and other sulphates are insoluble in alcohol, unless it be very dilute, and these salts may be precipitated by its free addition.

The formation of the yellow precipitate of *lead chromate*, from the white precipitate of sulphate (312), is a convenient confirmation. The solubility of the lead chromate in *fixed alkalies* distinguishes it from the yellow bismuth chromate (292), and the same reaction is a characteristic of the sulphate (see 449).

468. The precipitation by *water*, in this section of the group, is characteristic for **bismuth** (288). The *reduction* of the precipitated hydrate by sugar and fixed alkali, with black color (297), distinguishes bismuth from lead and from copper, the latter being thereby reduced with a reddish-brown color (280).

469. Owing to the waste of **copper** sulphide by ammonium sulphide, discussed in 457, a rigid analysis for this metal is most easily accomplished by examination of the original solution, or of the filtrate from the first group, by reduction with iron, or iron and platinum, according to 280.

The reduced copper may be dissolved by nitric acid, for further reactions.

470. The **Table** directs the test for **cadmium**, by hydrosulphuric acid, in the ammoniacal solution, which may contain copper or cadmium, or both. Now, both copper and cadmium are precipitated as sulphides in alkaline solutions (276 and 301); if the precipitate is yellow, it cannot contain much cupric sulphide; if it is black, it may consist largely of cadmic sulphide. But we have two agents capable of readily separating **CuS** from **CdS** (276):

Solution of potassium cyanide dissolves **CuS**, and leaves **CdS** undissolved.

Hot dilute sulphuric acid dissolves **CdS**, and leaves **CuS** undissolved.

471. The separation of **mercury**, by the insolubility of its sulphide with nitric acid (455, portion 3) is generally satisfactory, but it is not rigorously exact. There is usually an excess of sulphur with it, but the color of **HgS** is intense enough to blacken a large quantity of sulphur. This precipitate may be treated with carbon disulphide to dissolve away the free sulphur; then dried, mixed with sodium carbonate, and sublimed in a small glass tube closed at one end (363), with good results.

The solution with chlorine is generally tested by *reduction*, most often with stannous chloride. Reduction requires, as a matter of course, that the excess of chlorine should first be expelled.

The test by *ammonium hydrate* (347 and 357) is exceedingly delicate for mercury—in either class of combinations—though, of course, not characteristic to the eye. It may be used, in any solution, to confirm the absence of mercury.

472. Plan for separating the Bases without the use of Hydrosulphuric Acid or Ammonium Sulphide.*

The solution (*a*) may contain salts of:

I.—**Pb, Ag, Hg_2''**;
II.—**Ca, Ba, Sr**;
III.—**NH_4, Na, K**;
IV.—**As, Sb, Sn, Hg'', Cu, Cd, Bi**;
V.—**Fe, Cr, Al**;
VI.—**Mn, Mg, Co, Ni**;
VII.—**Zn**.

Add *hydrochloric acid* to the solution (*a*); agitate, filter, and wash.

Precipitate (*b*): (**$PbCl_2$**); **AgCl**; **Hg_2Cl_2**.

Solution (*c*): Salts in solution (*a*), except **Ag** and **Hg_2''**.

* Zettnow: *Poggendorff's Annalen*, 130, p. 324; *Zeitsch. f. anal. Chem.*, VI. (1867), 438; *Watts' Dictionary*, First Supplement, 124. Arranged in tabular form, by H. C. Bolton; *Amer. Chem.*, III. (1873), 452.

The *lead* in precipitate (*b*) is separated by *hot water* and filtration, then precipitated with sulphuric acid, etc. The **silver** is dissolved by *ammonium hydrate*, and reprecipitated by nitric acid; leaving the **mercury** as a black residue, insoluble in ammonium hydrate, but soluble in nitro-hydrochloric acid.

The solution (*c*) is treated with excess of dilute *sulphuric acid;* the precipitate filtered out and washed.

Precipitate (*d*): **$CaSO_4$; $BaSO_4$; $SrSO_4$; ($PbSO_4$).**

Solution (*e*): Classes III., IV., V., VI., and VII., of solution (*a*).

From precipitate (*d*)—the **calcium** sulphate is dissolved by agitation with *cold water*, and then precipitated by ammonium *oxalate*. See further, for calcium, under filtrate (*k*). Then, the **lead** sulphate is dissolved out by solution of *ammonium tartrate* with ammonium hydrate, the solution acidulated with acetic acid and precipitated by *chromate*. The residue—insoluble in water and in ammonium tartrate—contains the **barium and strontium** sulphates. [These may be separated by first transforming them into carbonates, by boiling with sodium carbonate, filtering, and washing out the sodium sulphate; then dissolving the carbonates in *hydrochloric acid*, evaporating to dryness, digesting in *absolute alcohol*, and filtering. The residue of **barium** chloride, free from alcohol, dissolved in water, should be precipitated by *solution of strontium sulphate*. The alcohol solution (**strontium** chloride) may be tested for strontium with the *flame*.]

Solution (*e*) is divided into a ¼ part and a ¾ part. The smaller part is tested for **the alkalies**, as follows:

Ammonia is detected in vapor, on adding excess of *solution of barium hydrate*, and boiling. The barium is then removed by precipitation with ammonium carbonate (or dilute sulphuric acid), filtering and igniting the evaporated filtrate. The residue is examined for **potassium** and **sodium**, by *flame colors*, both with and without blue glass.

The ¾ part of solution (*e*) has yet to be tested for classes IV., V., VI., and VII.: **As, Sb, Sn, Hg″, Cu, Cd, Bi; Fe, Cr, Al; Mn, Mg, Co, Ni; Zn.**

This portion of solution (*e*)—left with the excess of sulphuric acid from formation of precipitate (*d*)—is treated with *zinc* and *a piece of platinum foil in Marsh's apparatus*. The evolved gas is tested for arsenic and antimony—more perfectly by conducting it into solution of silver nitrate, and proceeding as elsewhere provided. The zinc will reduce the remaining metals of the fourth class.

Heat the generating flask ten or fifteen minutes, and filter.

Deposit (*f*): **Sb, Sn, Hg, Cu, Cd, Bi.**

Filtrate (*g*): **Fe, Cr, Al; Mn, Mg, Co, Ni; Zn** (as sulphates).

Deposit (*f*), well washed, is treated in an evaporating dish with *strong nitric acid*, and filtered.

Solution (*h*): Nitrates of **Hg, Bi, Cu,** and **Cd.**

Residue (*i*): **(Sb_2O_5), SnO_2.**

Test half of solution (*h*) with *stannous chloride* for **Mercury.** To the other half add hydrochloric acid, and boil; then add *excess of sodium hydrate*. The precipitated hydrates of bismuth, copper, and cadmium, are treated on the filter (after washing) with *ammonium hydrate* and *ammonium*

chloride. The **bismuth** is left undissolved;* the **copper** and **cadmium** in their ammonia solutions. The copper is recognized by its color, and by precipitation with *ferrocyanide*, after acidulation. The cadmium is distinguished from copper by precipitation by *sodium hydrate in the ammoniacal solution.*†

Residue (*i*) is washed, and boiled with *hydrochloric acid*, which dissolves the antimonic acid, and leaves the metastannic acid undissolved. The solution is tested with *platinum and zinc* for **antimony.** The residue is dissolved, with action of nascent hydrogen, by *hydrochloric acid with zinc*, and tested with *mercuric chloride* for **tin.**

Treat filtrate (*g*) with *nitric acid*, for oxidation. Test a small portion with *sulphocyanate*, for **iron.** Treat the remaining portion with *barium carbonate* (after neutralizing with ammonia); digest for some time, and filter.‡

Precipitate (*j*): $Cr_2(OH)_6$, $Al_2(OH)_6$, with $Fe_2(OH)_6$, and excess of $BaCO_3$.

Filtrate (*k*): **Mn, Mg, Co, Ni; Zn** (as sulphates).

Treat precipitate (*j*) with dilute sulphuric acid, to remove the barium, and filter. Boil the filtrate to expel carbonic anhydride; then boil with *excess of sodium hydrate*, and digest with a little *potassium permanganate* to oxidize the chromium to chromate. Test a portion of this soda solution with *lead acetate* (after acidulation with acetic acid) for **chromium.** Treat another portion with *ammonium chloride* in excess for precipitation of **aluminium.**§

From filtrate (*k*), remove the barium by adding a very slight excess of sulphuric acid, and filtering; then add *ammonium carbonate* in slight excess to precipitate **manganese**, and filter. Test a portion of the precipitate for manganese. by fusion with *sodium nitrate* and *carbonate.* Treat another portion for **calcium**, which escapes precipitate *d*, by adding ammonium hydrate to neutralize; then much *ammonium chloride*, and *ammonium oxalate.* To the filtrate, add *sodium phosphate* to precipitate **magnesium**, and filter. Evaporate the filtrate to dryness; it may contain cobalt and nickel. Dissolve it in hydrochloric acid, and add *potassium nitrite and acetic acid* and leave some hours to precipitate **cobalt**, and filter. To the filtrate, add *sodium hydrate*, for the precipitation of **nickel.**

To test for **zinc** (*seventh class*), take a portion of solution (*e*)—or prepare it anew from the original solution by treatment, successively, with sulphuric and hydrochloric acids and filtration; and warm with *excess of sodium hydrate*, and filter.¶ The filtrate (sodium zincate) is nearly neutralized with *ammonic carbonate*, and treated with *ammonic chloride* as long as ammonia escapes, and again filtered. The last filtrate is tested with *potassium ferrocyanide* for a precipitate of **zinc.**

* The residue is dissolved in *hydrochloric acid*, and the solution treated with much *water*, for the more certain determination of **bismuth.**

† In case that much copper is present, the test for **cadmium** is better made as follows: The solution is strongly acidulated with *hydrochloric acid*, and boiled; then, while hot, treated with successive small additions of solution of *sodium thiosulphate*, to completion of the black precipitate, the liquid being milky with sulphur. After filtration, the filtrate is tested by sodium hydrate for cadmium.

‡ If the presence of phosphoric acid is to be provided for, add sufficient *ferric chloride*, and digest before neutralizing and adding barium carbonate.

§ Manganese, and even other metals belonging in filtrate *k*, may be precipitated from their sulphates by barium carbonate, in absence of *sufficient* ammonium chloride.

¶ Zettnow directs to "boil" with the excess of sodium hydrate, but this is liable to precipitate zinc.

GOLD.

473. Gold is not tarnished or affected by air or water at any temperature, or by hydrosulphuric acid. Neither nitric nor hydrochloric acid attacks it under any conditions; but it is rapidly attacked in vapor or solution by **chlorine**, dissolving promptly in nitro-hydrochloric acid, as *auric chloride*, $AuCl_3$; by **bromine**, dissolving in bromine water, as *auric bromide*, $AuBr_3$; and by **iodine**, dissolving when finely divided in hydriodic acid by aid of the air and potassium iodide, as *potassium auric iodide*, $KIAuI_3$ (*a*). **Cyanide** of potassium solution, with aid of the air, dissolves precipitated gold as potassium *aurocyanide*, $KAuCy_2$ (*b*):

a. $2Au + 6HI + 2KI + 3O = 2KIAuI_3 + 3H_2O$

b. $2Au + 4KCy + O + H_2O = 2KAuCy_2 + 2KOH$

474. Gold forms two *oxides: aurous*, Au'_2O, and *auric*, Au'''_2O_3; but forms no stable oxy-salts. It forms the two classes of haloid salts, corresponding to the oxides. The aurous *chloride*, $AuCl$, and *other* aurous salts, are either insoluble in water or decomposed by water with partial solution and separation of gold, $3AuCl = 2Au + AuCl_3$. —The auric *chloride*, $AuCl_3$, and bromide, are soluble in water; the iodide decomposed by water, with precipitation of yellow aurous iodide; the sulphide insoluble in water. There are many double salts of gold and alkali metals, mostly soluble in water: double chlorides and iodides; aurocyanides, as NH_4AuCy_2, and auricyanides, as $KAuCy_4$; and a sodio aurous thiosulphate, $Na_3Au(S_2O_3)_2$, soluble in water.

Gold is most readily **separated** and distinguished by reduction to the metallic state.

475. Fixed **alkali hydrates** do not precipitate solution of auric chloride; ammonium hydrate precipitates, in concentrated solution, a reddish-yellow *ammonia aurate*, $(NH_3)_2Au_2O_3$, "fulminating gold." — **Hydrosulphuric acid**, and sulphides, give, in cold solutions, a black precipitate of *auric sulphide*, Au_2S_3; in boiling changed to *aurous sulphide*, Au_2S, brown. These sulphides are slowly **soluble in yellow alkali sulphides**, forming alkali *sulphaurates*, as Na_3AuS_3; not soluble in colorless alkali sulphides; soluble in nitro-hydrochloric, not in nitric or hydrochloric acid. Acids reprecipitate auric sulphide from the sulphaurate solution.

Potassium iodide, added in small portions *to* solution of auric chloride (so that the latter is constantly in excess where the two salts are in contact), and when equivalent proportions have been reached, gives a yellow precipitate of *aurous iodide*, AuI, insoluble in water, soluble in large excess of the reagent; the precipitate accompanied with separation of free iodine, brown, which is quickly soluble in small excess of the reagent as a colored solution [$AuCl_3 + 4KI = AuI + 3KCl + 2I$ with KI]. But, on gradually adding auric chloride to solution of potassic iodide, so that the latter is in excess at the point of chemical change, there is first a dark-green solution of potassio auric iodide, $KIAuI_3$; then a dark-green precipitate of *auric iodide*, AuI_3, very instable, decomposed in pure water, more quickly by boiling; changed in the air to the yellow aurous iodide.

All **reducing agents** are oxidized by auric chloride, with precipitation of *gold*—at first of a brown to a violet color, acquiring, when triturated, the color and lustre which distinguish it in mass. The metals, and all lower oxides and salts, reduce gold. **Ferrous** sulphate forms it in brown precipitate; **stannous chloride** gives a purple precipitate, "purple of Cassius," Au_2O, containing the oxides of tin:

$$2AuCl_3 + 6FeCl_2 = 2Au + 3Fe_2Cl_6$$

476. Gold is reduced from many of its compounds by **light**, and from all of them by **heat**—its separation **in the dry way** being readily effected by fusion with such reagents as will make the material fusible. Very small proportions are collected in alloy with lead, by fusion; after which the lead is vaporized in "cupellation," as described for silver (341).

477. Gold is separated, from its alloys with silver and base metals, by solution in **nitric acid**; the gold being left as a black-brown powder—together with platinum and oxides of antimony and tin. When the gold-silver or gold-copper has not over 20 p. c. gold, nitric acid of 20 p. c. disintegrates the alloy, and effects the separation; when the gold is over 25 p. c., silver or lead (three parts) must be added, by fusion, to the alloy before solution. (If gold-silver alloy contains 60 p. c. or more of silver, it is silver-color; if 30 p. c. silver, a light brass-color; if 2 p. c. silver, it is brass-color.)

If gold and other metals are obtained in solution by **nitro-hydrochloric acid**, leaving most of the silver as a residue, the noble metals can be precipitated by zinc or ferrous sulphate, and the *precipitate* of gold, silver, etc., treated with nitric acid, which will now dissolve out any proportion of silver not less than 15 p. c., to 85 p. c. of gold, and dissolve the baser metals. Concentrated **sulphuric acid** dissolves silver, and leaves gold.

Oxalic acid reduces gold from solution, not too strongly acid, slowly but completely. To the auric chloride, it is better to add both ammonium oxalate and oxalic acid. Platinum, palladium, and the second group metals are not reduced by oxalic acid; hence, whenever the systematic analysis of a solution is made to include gold, this metal should be tested for and *removed by oxalic acid, before the first and second group precipitations.*

PLATINUM.

478. A tin-white **metal**, nearly as lustrous as silver, fusible in the oxy-hydrogen blow-pipe flame, by which it can be vaporized. It is obtained as a soot-black powder—"platinum-black"—by reduction from solution of alkali and alcohol; and as a gray, porous, slightly coherent mass—"platinum-sponge"—by ignition of ammonio-platinic chloride. Both these bodies are remarkable for adhesive power; and both, by strong compression, become compact, malleable, and lustrous, in the ordinary form of the metal. Platinum is not affected by air or water, at any temperature; is not sensibly **tarnished** by hydrosulphuric acid vapor or solution; and is not attacked at any temperature by

nitric acid, hydrochloric acid, or sulphuric acid, but dissolves in **nitro-hydrochloric** acid, to platinic chloride, less readily than gold.

479. The **Preservation of Platinum Vessels** requires that it be remembered: (1) That free *chlorine* and *bromine* attack platinum at ordinary temperatures (forming platinic chloride, bromide); and free *sulphur*, *phosphorus*, arsenic, *selenium*, and iodine, attack *ignited* platinum (forming platinous sulphide, platinic phosphide, platinum-arsenic alloy, platinic selenide, iodide). Hence, the fusion of sulphides, sulphates, and phosphates, *with reducing agents*, is detrimental or fatal to platinum crucibles. The ignition of organic substance containing phosphates acts as free phosphorus, in a slight degree.

The heating of ferric chloride, and the fusion of bromides, and iodides, act to some extent on platinum.

(2.) The *alkali hydrates* (not their carbonates) and the alkaline-earths, especially baryta and lithia, with *ignited* platinum *in the air*, gradually corrode platinum (by formation of platinites: **Pt + BaO + O = BaO.PtO**).

(3.) All **metals** *which may be reduced in the fusion—especially compounds of lead, bismuth, tin*, and other metals easily reduced and melted—and all *metallic compounds with reducing agents* (including even alkalies and earths) form fusible alloys with ignited platinum. Mercury, lead, bismuth, tin, antimony, zinc, etc., are liable to be rapidly reduced, and *immediately to melt away platinum* in contact with them.

(4.) *Silica with charcoal* (by formation of silicide of platinum) corrodes ignited platinum, though very slowly. Therefore, platinum crucibles should not be supported on charcoal in the furnace, but in a bed of magnesia, in an outer crucible of clay. Over the flame, the best support is the triangle of platinum wire.

(5.) The tarnish of the gas-flame increases far more rapidly upon the already tarnished surface of platinum—going on to corrosion and cracking. The surface should be kept polished—preferably by gentle rubbing with moist *sea-sand* (the grains of which are perfectly rounded, and *do not scratch* the metal). Platinum surfaces are also **cleansed** by fusing *borax* upon them, and by digestion with nitric acid.

480. Platinum forms two **oxides**, platinous oxide, $Pt''O$, and platinic oxide, $Pt''''O_2$,—both of which represent corresponding classes of oxy-salts and haloid salts. The oxy-salts are instable.—None of the **platinous** compounds are permanently **soluble** in pure water; the chloride is soluble in hydrochloric acid, the sulphate in water acidulated with sulphuric acid.—**Platinic** *chloride* ($PtCl_4$) and bromide, all the platinicyanides (as $PbPtCy_6$), and the platinocyanides of the metals of the alkalies and alkaline earths (as K_2PtCy_4), are **soluble** in water. The platinous and platinic nitrates are soluble in water, but easily decomposed by it, with the precipitation of basic salts. The larger number of the *metallo-platinic chlorides* or "chloroplatinates" are soluble in water, including those with sodium [Na_2PtCl_6 or $(NaCl)_2PtCl_4$], barium, strontium, magnesium, zinc, aluminium, copper; and those with potassium, and ammonium, are sparingly soluble in water, and owe their analytical importance as complete precipitates (40) to their insolubility

in alcohol. Of the *metallo-platinous chlorides* (the "chloroplatinites")—those with sodium [Na_2PtCl_4 or $(NaCl)_2PtCl_2$], and barium, are soluble; zinc, potassium, and ammonium, sparingly soluble; lead and silver, insoluble in water. Platinic *sulphate*, $Pt(SO_4)_2$, is soluble in water.

481. Platinous chloride, $PtCl_2$, is a greenish-brown powder, soluble in hydrochloric acid without change, as a dark-brown solution, which remains platinous if protected from the air, but becomes platinic in contact with the air. The purely platinous chloride solution is precipitated by **potassium hydrate** and sodium hydrate as *platinous hydrate*, $Pt(OH)_2$, dark-brown, soluble in excess, as alkali platinite, $K_2O.PtO$, etc.; from which alkaline solutions, alcohol precipitates "platinum black" (478).—**Ammonium hydrate** gives a green crystalline precipitate of *platino-diammonium chloride*, $N_2H_6PtCl_2$, insoluble in cold water and in alcohol (compare 347). **Hydrosulphuric acid** very slowly precipitates *platinous sulphide*, **PtS**, black, sparingly soluble in water, not affected by the acids or chlorine or potassium hydrate, sparingly **soluble by ammonium sulphide.**—**Iodide** of potassium slowly precipitates *platinous iodide*, PtI_2, red-brown to black.—Oxalic acid produces no change; **ferrous** sulphate (slowly), and **zinc** (quickly), reduce the *metal.*

482. Platinic Chloride, $PtCl_4$, is a brown-red solid, dissolving in water, or alcohol, as a reddish-yellow solution, permanent in the air.—**Potassium hydrate,** and **ammonium hydrate,** give, in solutions not very dilute, a yellow crystalline precipitate, as *potassium platinic chloride*, or potassium chloroplatinate, $(KCl)_2PtCl_4$, etc., slightly soluble in water, insoluble in alcohol, soluble in excess of the alkalies, and reprecipitated by hydrochloric acid. **Chlorides** of potassium and ammonium give the precipitate, the most nearly complete. **Carbonates** of potassium and ammonium form the same precipitates, insoluble in excess. Sodium carbonate gives no precipitate. **Sodium hydrate** slowly precipitates, in moderately concentrated solutions, after warming, the (brownish-yellow) sodium platinate, $Na_2O.PtO_2$.—Potassium **iodide** colors the solution brown-red, and precipitates the black *platinic iodide*, PtI_4; with excess of the reagent, forming the sparingly soluble *potassium platinic iodide*, $(KI)_2PtI_4$, brown. Sodium iodide the same.—**Hydrosulphuric acid,** and ammonium sulphide, slowly precipitate the black *platinic sulphide*, PtS_2, slightly soluble in water, soluble by chlorine, and **soluble in ammonium sulphide,** as ammonium *sulphoplatinate;* sodium sulphoplatinate is likewise soluble, reprecipitated by acids. Phosphates form no precipitate. **Reduction** is not effected by oxalic acid (distinction from gold); is slowly accomplished by **ferrous** sulphate, and rapidly by **zinc**; also by **chloral hydrate,** and excess of **alkali** with heat (formiate); the reduced metal being, in each case, in black powder.—By the reducing **blow-pipe flame,** the compounds of platinum are reduced to *spongy platinum.*

PALLADIUM.

483. A white **metal**, more lustrous than platinum, with which it is classed, in accordance with its general properties. It is, however, a little more fusible and volatile (in the oxyhydrogen flame), and much more oxidizable than platinum. In the air, it is little tarnished at ordinary temperatures, but at a red heat it covers with oxide.—It is slightly attacked by boiling hydrochloric or sulphuric acid; dissolves in **nitric** acid, with formation of palladic nitrate, and if in the cold, with separation of nitrous acid, which remains in solution; more readily in **nitro-hydrochloric** acid, as palladic chloride, $PdCl_4$. It is blackened by alcoholic solution of **iodine** (distinction from platinum).

484. Palladium forms one stable oxide, palladious, **PdO**, and two chlorides, palladious, $PdCl_2$, and palladic, $PdCl_4$. The latter is the most stable of the palladic combinations, but is reduced to palladious chloride by boiling in water, and by dilution with much cold water.

485. **Palladious** *chloride* is readily soluble in water with a brownish-red color; with metallic chlorides, it forms double chlorides, as potassio palladious chloride or "potassium chloropalladite," $(KCl)_2PdCl_2$, all of which are soluble in water.—Palladious *iodide* is insoluble in water, alcohol, or ether; insoluble in dilute hydrochloric acid or hydriodic acid; slightly soluble by iodides and by chlorides.—Palladious *nitrate*, $Pd(NO_3)_2$, is soluble in water with free nitric acid; the solution being decomposed by dilution, evaporation, or by standing, with precipitation of variable basic nitrates. Palladious sulphate, $PdSO_4$, dissolves in water, but decomposes in solution on standing.

The instable **palladic** *chloride*, brown-black in solution, forms double chlorides with the metals—as calcio palladic chloride or "calcium chloropalladiate," $CaCl_2PdCl_4$—these being mostly stable in water, and mostly soluble in water and in alcohol. The potassium palladic chloride (red), as an exception, is slightly soluble in water and insoluble in alcohol, but partially decomposed by both solvents.

486. **Palladious Chloride** is precipitated by **potassium hydrate** or **sodium hydrate**, as brown basic salt or as brown *palladious hydrate*, $Pd(OH)_2$, soluble in excess of the hot reagents. **Ammonium hydrate** gives a flesh-red precipitate of *palladio-diammonium chloride*, $N_2H_6PdCl_2$ (compare 347). The flesh-red precipitate is soluble in excess of the ammonia, and from this solution reprecipitated by hydrochloric acid, with a yellow color. The fixed alkali **carbonates** precipitate the hydrate; ammonium carbonate acts like the hydrate.—**Hydrosulphuric acid** and sulphides precipitate the dark-brown *palladious cyanide*, **PdS, insoluble in the ammonium sulphides**, soluble in nitro-hydrochloric acid. —Potassium **iodide** precipitates *palladious iodide*, PdI_2, black, visible in 500,000 parts of the solution, with the slight solubilities stated in 485, an important separation of iodine from bromine. In very dilute solutions, only a color is produced, or the precipitate separates after warming. At a red heat, the precipitate is decomposed. Potassium **cyanide** precipitates *palladious cyanide*, $PdCy_2$, white, soluble in excess of the reagent. —**Chloride** of **potassium** precipitates, from highly concentrated solutions, the golden-yellow, crystalline, *potassium palladious chloride*, $(KCl)_2PdCl_2$ (485). **Phosphates** give a brown precipitate.

Palladious nitrate gives most of the above reactions; no precipitate with ammonia, and a less complete precipitate with iodides.

487. Palladium is **reduced**, in dark-colored precipitate, from all compounds in solution, by **sulphurous acid**, stannous chloride, phosphorus, and all the metals, which precipitate silver (340). Ferrous sulphate reduces palladium from its nitrate, not from its chloride. Alcohol, at boiling heat, reduces it; oxalic acid does not (distinction from gold).

—Nearly all its compounds are reduced by heat, before the blow-pipe, to a "sponge." If this be held in the inner flame of an alcohol-lamp, it absorbs carbon at a heat below redness ; if then removed from the flame, it glows vividly in the air, till the carbon is all burnt away (distinction from platinum).

MOLYBDENUM.

488. A silver-white, hard and brittle **metal**, fusible at the highest furnace heat. It is not **oxidized** in the air at ordinary temperatures; but when slowly heated, it gains a brownish-yellow, then a blue tarnish ; and at a higher heat, it burns to MoO_3. It is oxidized by water vapor at a red heat. It is quickly **dissolved** by **nitric acid**, as molybdic anhydride (MoO_3), with evolution of nitric oxide; slowly by hot, strong sulphuric acid, with liberation of sulphurous anhydride. Molybdenum forms three **classes of compounds**, viz., *molybdous* oxide, $Mo''O$; chloride, $MoCl_2$, and other molybdous salts ; *molybdic* oxide, $Mo''''O_2$; chloride, $MoCl_4$, and corresponding salts ; and molybdic *anhydride*, $Mo^{VI}O_3$, which combines with bases, to form stable molybdates—also feebly unites with strong acids. Each of these classes includes stable salts; the two bases are converted into molybdic acid or molybdates by strong oxidizing agents; while molybdates are reducible to one or the other of the bases by deoxidizing agents.

489. The *molybdous* salts are not generally very permanent in **solution.** The chloride is soluble (in dilute hydrochloric acid ?); the bromide and iodide decomposed in water to oxybromide and oxiodide; the sulphate decomposed by water to a soluble and an insoluble salt; the nitrate soluble in water. The solutions are dark-brown and opaque.

Water **dissolves** *molybdic* chloride, bromide (yellow-brown solution), iodide (red solution), nitrate and sulphate (reddish-brown solutions).

Molybdic *anhydride* is very sparingly **soluble** in water (800 parts). It does not form an acid in the solid state. The normal *molybdates* of the alkali metals (as K_2MoO_4) are soluble, of the remaining metals insoluble in water. The molybdenum trisulphate, $Mo(SO_4)_3$, and molybdenum hexi-chloride $MoCl_6$, are soluble in water; the corresponding nitrate, $Mo(NO_3)_6$, soluble in dilute nitric acid.

490. Molybdous salts, as $Mo(NO_3)_2$, with **alkali hydrates** and **carbonates**, precipitate the dark-brown *molybdous hydrate*, becoming *blue* in the **air** by oxidation to molybdic molybdate, $Mo(MoO_4)_2$ and Mo_2O_5. The hydrate is insoluble in alkalies, sparingly soluble in alkali carbonates, readily soluble in alkali hydrogen carbonates. With **hydrosulphuric acid** and **sulphides**, a brown precipitate of *molybdous sulphide*, **MoS, soluble in ammonium sulphide.**

491. Molybdic salts, as $MoCl_4$, with **alkali hydrates** and **sulphides**, give reactions corresponding with molybdous salts, and likewise turn *blue* in the **air,** by formation of intermediate oxides. The precipitated hydrate is reddish-brown; it dissolves in alkali carbonates by formation of alkali molybdates. **Zinc** precipitates *molybdous hydrate*, by reduction.

492. Molybdic **Anhydride** is a white powder, or is in needle-form crystals, turning yellow when hot and again white on cooling; melting at a red and vaporizing at a white heat. It is soluble by acids, and by alkali-hydrates, especially ammonia, in formation of molybdates.

493. Water solutions of **MOLYBDATES**, with acids, precipitate molybdic

anhydride, MoO_3, white, soluble in excess of the acids.* **Hydrosulphuric acid** colors the molybdate in neutral or alkaline solutions, yellow to brown, without precipitation; but from the acid solutions it precipitates the brown MoS_2, *sulphomolybdic acid*, the supernatent liquid appearing blue. The precipitate is **soluble in ammonium sulphide**, better when hot and not too concentrated, as ammonium sulphomolybdate, $(NH_4)_2MoS_4$, from which acids reprecipitate MoS_3.

494. Tribasic **phosphoric acid** and its salts precipitate, from strong nitric acid solutions of ammonium molybdate, somewhat slowly and on warming, *ammonium phosphomolybdate*, yellow, of variable composition, soluble in ammonia and other alkalies, sparingly soluble in excess of the phosphate. Hydrochloric acid may be used instead of nitric. The *sodium phosphomolybdate* is soluble in water, and precipitates ammonium from its salts; also, it precipitates the alkaloids—for which reaction it has some importance as a reagent.† (Compare Ammonium, 62.)

Arsenic acid and **arseniates** give the same reaction; *ammonium arsenomolybdate* being formed.

Recent molybdic anhydride, well washed (with alcohol and then water), on digestion with aqueous phosphoric acid, forms a lemon-yellow salt, insoluble in water, but slowly soluble in excess of the hot phosphoric acid, as acid permolybdic phosphate or *phosphomolybdic acid.* It is soluble in alcohol as well as in water; the solution giving, with ammonia and with alkaloids, the yellow precipitate of ammonium phosphomolybdate, etc.

495. The alkaline solutions—normal molybdates of the alkali metals—give, with all **non-alkali salts**, precipitates of non-alkali molybdates, the latter being insoluble (or sparingly soluble) in water, as stated in 489. The following are some of the reactions giving precipitates:

K_2MoO_4	+	$BaCl_2$	=	$BaMoO_4$	+	$2KCl$
K_2MoO_4	+	$Pb(NO_3)_2$	=	$PbMoO_4$ (wulfenite)	+	$2KNO_3$
K_2MoO_4	+	$CuSO_4$	=	$CuMoO_4$ (yellow-green)	+	K_2SO_4

496. Reducing agents convert molybdic acid either into the *blue* intermediate oxides (490), or, by further deoxidation, into the *black* molybdous oxide, MoO. In the (hydrochloric) acid solutions of molybdic acid, the blue or black oxide formed by reduction, will be held in solution with a blue or

* In making the solution of molybdate with nitric acid, used as a reagent, the slightly alkaline solution of the molybdate is poured into the nitric acid, slowly, with stirring.

† *Sodium Phosphomolybdate*—Sonnenschein's reagent for acid solutions of alkaloids—is prepared as follows: The yellow precipitate formed on mixing acid solutions of ammonium molybdate and sodium phosphate—the ammonium phosphomolybdate—is well washed, suspended in water, and heated with sodium carbonate until completely dissolved. The solution is evaporated to dryness, and the residue gently ignited till all ammonia is expelled, sodium being substituted for ammonium. If blackening occurs, from reduction of molybdenum, the residue is moistened with nitric acid, and heated again. It is then dissolved with water and nitric acid to strong acidulation; the solution being made ten parts to one part of residue. It must be kept from contact with vapor of ammonia, both during the preparation and when preserved for use.

brown color. Nitric acidulation is, of course, incompatible with the reduction. Certain reducing agents act as follows:

Ferrous salts (in the hydrochloric acid solution) give the *blue* oxide solution. **Cane sugar**, in the feebly acid boiling solution, forms the *blue* color —seen better after dilution; a delicate test. **Stannous chloride** forms first the *blue*, then the *brown*, or the *greenish*-brown to black-brown, solution of both the intermediate oxide and the molybdous oxide. **Zinc** gives the *blue*, then *green*, then *brown* color, by progressive reduction. Formic and oxalic acids do not react.—Dry molybdates, heated on platinum foil with concentrated sulphuric acid to vaporization of the latter, form, on cooling in the air, a *blue* mass—a very delicate test.*

497. With microcosmic salt, in the outer blow-pipe flame, all compounds of molybdenum give a bead which is greenish while hot, and colorless on cooling; in the inner flame, a clear green bead. With borax, in the outer flame, a bead, yellow while hot, and colorless on cooling; in the inner flame, a brown bead, opaque if strongly saturated (molybdous oxide). On charcoal, in the outer flame, molybdic anhydride is vaporized as a white incrustation; in the inner flame (better with sodium carbonate), metallic molybdenum is obtained as a gray powder, separated from the mass by levigation.

* A solution of 1 milligram of sodium (or ammonium) molybdate in 1 c.c. of concentrated sulphuric acid (about 1 part to 1.840 parts) is in use as Fröhde's Reagent for alkaloids. The molybdenum in this solution, which must be freshly prepared for use each time, is reduced by very many organic substances; and with a large number of alkaloids, it gives distinctive colors, blue, red, brown, and yellow.

498. Reactions of Ruthenium, Iridium, Rhodium, and Osmium.

In solution as	Ru_2Cl_6, orange.	$(NaCl)_2IrCl_4$, black.	$K_3Rh(SO_4)_3$, rose-colored.	$(KCl)_8Os_8Cl_6$, sparingly soluble.
H_2S, in acid sol.	Ru_2S_3, brown, formed slowly, with blue sol.	$Ir_2S_3 + S$, brown.	Rh_2S_3, brown, sol. in hot nitric acid.	OsS, brown, formed only by strong acid.
$(NH_4)_2S_2$, in excess.	Solution formed with difficulty.	Solution.	Precipitate.	Precipitate.
KOH or NaOH, in excess.	$Ru_2(OH)_6$, black.	Brown-black pre., turning blue.	Solution, pre. by alcohol.	$Os(OH)_4$, brown-red.
$SnCl_2$.	. . . . .	$(NaCl)_6Ir_2Cl_6$.	. . . . .	Brown pre.
Zn.	Pre., blue to black.	Ir, black.	Rh, black.	Os.
KNO_2.	Pre., sol. in excess, turned to dark-red by $(NH_4)_2S$.	$Ir(OH)_4 + KNO_2$, boiled with SO_2, green pre.	Pre., orange.	No change.
	(1)	(2)	(3)	(4)

(1) **Potassium sulphocyanate**, in absence of other platinum metals, slowly forms a *red color*, turning to violet when boiled.

(2) The metal is insoluble in all **acids**. After fusion with sodium hydrate and oxidizing agents, it dissolves by nitro-hydrochloric acid.

(3) The metal is insoluble in all acids; but by fusion with potassium hydrogen sulphate, forms the soluble salt above taken.

(4) The metal vaporizes at white heat, and burns to OsO_4, an acidulous anhydride, having an irritating and offensive odor, and forming instable *osmates* of great oxidizing power. Osmates separate iodine from iodides, decolorize indigo solution, and, with **sulphites**, give a deep violet color or blue precipitate.

499. Reactions of Tellurium, Selenium, and Tungsten.

In solution as	K_2TeO_3.	K_2TeO_4.	Na_2SeO_3.	Na_2SeO_4.	Na_2WO_4.
H_2S in acid sol.	TeS_2, brown.	. . . .	SeS_2.	. . . .	Blue solution, W_2O_5.
$(NH_4)_2S_2$, excess.	No pre.	. . . .	No pre.	. . . .	No pre.
HCl.	H_2TeO_3, white pre.	Boiled. H_2TeO_3, and Cl.	No pre.	Boiled, H_2SeO_3, and Cl.	H_2WO_4, white pre., then yellow.
$SnCl_2$.	Te, black.	. . . .	Se, red.	. . . .	Yellow pre., heated with HCl, blue.
Fusion on Ch, with Na_2CO_3.	Na_2Te, staining Ag, and with acids giving H_2Te, having odor of H_2S, and dissolving red.		Na_2Se, staining Ag, and with acids giving H_2Se, of fœtid odor, soluble in water.		W, black.
	(1)	(2)	(3)	(4)	(5)

(1) The *tellurites* of the alkali and alkaline earthy metals are soluble in water, the other tellurites insoluble.

(2) The *tellurates* of the alkali metals, alone, are soluble in water.

(3) Except those of the alkali metals, the *selenites* are insoluble in water.

(4) Lead, barium, strontium, and calcium *selenates* are insoluble in water; other selenates, soluble. Barium selenate, insoluble in HCl.

(5) Of the *tungstates*, only those of the alkali bases dissolve in water.

PART II.

THE NON-METALS AND THE ACIDS.

---

500. The three elements, chlorine, bromine, and iodine, resemble each other in almost all their properties, reactions, and combinations, differing (as do their atomic weights, 35, 80, 127) with a regular progressive variation; so that their compounds present themselves to us as members of progressive series. In several particulars fluorine (atomic weight, 19) corresponds to the first member of this series.

501. CHLORINE is a greenish-yellow, suffocating gas, dissolved sparingly by cold water, very slightly by hot water. The solution bleaches litmus; but on standing, the **Cl** is converted into **HCl** (*a*), when it reddens litmus, and is no longer fit for use as a reagent. Chlorine is dissolved freely by alkali hydrates, with combination (*b*), the solution having especial oxidizing force (526). In *distinction from hydrochloric acid*, it bleaches moist **litmus**, and indigo solution; precipitates sulphur from hydrosulphuric acid, and iodine from solutions of iodides—slight traces of it being revealed by the blue color with solution of **potassium iodide** and **starch**—and acts in presence of water as *a very powerful oxidizing agent* (*a*). It displaces bromine, as well as iodine. It dissolves gold-leaf, and mercuric sulphide (*distinctions from nitric acid*). Like hydrochloric acid, it precipitates solution of silver nitrate (*c*), and plumbic and mercurous salts; and forms, with vapor of ammonia, a white cloud of NH_4Cl. With ammonium salts, chlorine is liable to cause explosion, nitrogen chloride being formed (63). For the Oxidations caused by chlorine, see 820.

a. $2Cl + H_2O = O + 2HCl$

b. $6Cl + 6KOH = 5KCl + KClO_3 + 3H_2O$

Or: $2Cl + 2KOH = KCl + KClO + H_2O$

c. $6Cl + 6AgNO_3 + 3H_2O = 5AgCl + AgClO_3 + 6HNO_3$

502. The most important **Acids containing Chlorine** are:

Hydrochloric acid, HCl'.
Chloric acid, $HCl^{V}O_3$.
Perchloric acid, $HCl^{VII}O_4$.
Hypochlorous acid, $HCl'O$.

HYDROCHLORIC ACID.

503. Absolute hydrochloric acid is a colorless, caustic, suffocating **gas.** It **dissolves** in about two parts by weight of water; so that its strongest permanent solution contains about 33 per cent. of acid (**HCl**); but this solution rapidly evolves acid in the air, more rapidly on warming, less rapidly as the solution loses strength. When of 20 per cent. acid, the liquid boils at 112° C. (233° F.), vaporizing with the water of its solution.

504. Gaseous hydrochloric acid escapes with slow **effervescence** when liberated from compounds in concentrated solution; reddens **litmus**; with vapor of **ammonia**, gives a white cloud (NH_4Cl as a solid), somewhat more dense than the fumes caused by the other volatile acids; and, like aqueous hydrochloric acid (508), precipitates chlorides from salts of the **first group metals**, when brought in contact with their solutions—a drop adhering to a glass rod being held in the gas.

505. Hydrochloric acid is formed from metallic chlorides by transposition with **sulphuric acid**; except that mercury, silver, lead, and tin chlorides are transposed with difficulty, or not at all, by sulphuric acid:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

506. The normal *Chlorides* are all **soluble in water**, except those of the metals of the first group; silver, **AgCl**; mercurous, Hg_2Cl_2; and lead, $PbCl_2$—the last named being sparingly soluble. In **analysis**, the silver precipitate is most used (509). If bromides are present (535), the chlorochromic test is most conclusive (512). Separation from iodides, 577.

A large number of the metallic chlorides are soluble in alcohol, and several are soluble in ether.

507. The chlorides of metals are, generally, more **volatile** than other compounds of the sample metals; example, ferric chloride.

508. Solutions of chlorides and hydrochloric acid are precipitated, by solutions of **silver salts**, as *silver chloride*, **AgCl**, white (332); by solutions of **mercurous salts**, as *mercurous chloride*, Hg_2Cl_2, white (350); and by solutions of **lead salts**, when not very dilute, as *lead chloride*, $PbCl_2$, white (313). **Silver nitrate** solution is the most complete and convenient precipitant for chlorides.

509. The properties of the precipitate of *silver chloride* are given in 332, and in 328. It is of analytical interest, that it is freely soluble in **ammonium hydrate** (considerably more freely than the bromide, and far more freely than the iodide of silver); soluble in hot, concentrated solution of **ammonium carbonate** (which dissolves traces of bromide, and no iodide of silver); insoluble in nitric acid, or but temporarily soluble in strong nitric (as in hydrochloric) acid, and precipitating again on dilution. It should be observed, that

it is appreciably soluble in solutions of chlorides, and in ammonium nitrate; hence, in reprecipitating traces of it, by nitric acid, from the ammonia solution, if there is excess of ammonium hydrate, this should first be expelled:

$$2AgCl + 3NH_4OH = (NH_3)_3(AgCl)_2 + 3H_2O$$

$$(NH_3)_3(AgCl)_2 + 3HNO_3 = 2AgCl + 3NH_4NO_3$$

510. Oxidizing agents (with heat) *decompose hydrochloric acid, or metallic chlorides with an acid; chlorine being liberated,* by oxidation of the hydrogen of the hydrochloric acid or of the metal of the chloride. In this way, manganese dioxide (511), lead dioxide (306), chromic anhydride (512), nitric acid (513), and chlorates (522), produce chlorine from chlorides. For other reactions of Oxidizing Agents, see 821.

511. The action of *manganese dioxide* is formulated as follows:

$$4HCl + MnO_2 = MnCl_2 + 2H_2O + 2Cl$$

Or: $2NaCl + 2H_2SO_4 + MnO_2 = Na_2SO_4 + MnSO_4 + 2H_2O + 2Cl$

This reaction is applied in the manufacture of chlorine, which is distilled from the mixture, and can be used in analysis for evidence of chlorides.

A test for *traces of free hydrochloric acid,* in distinction from metallic chlorides, is made by heating the solution with MnO_2, without adding an acid, and distilling into a solution of potassium iodide and starch. Larger proportions of HCl are more frequently separated by distilling it intact.

512. The reaction with *chromic anhydride* is in use as a test for hydrochloric acid, more especially in presence of bromides:

a. $2HCl + CrO_3 = CrO_2Cl_2$ (chlorochromic anhydride) $+ H_2O$

b. $4NaCl + K_2Cr_2O_7 + 3H_2SO_4 =$

$$2CrO_2Cl_2 + 2Na_2SO_4 + K_2SO_4 + 3H_2O$$

To obtain a rapid production of the gas, so that it may be recognized by its color, the operation may be made as follows: Boil a mixture of solid **potassium dichromate** and **sulphuric acid**, in an evaporating dish until bright red, and then add the substance to be tested, in powder—obtained, if necessary, by evaporation of the solution. If chlorides are present, the chromium dioxy-dichloride rises instantly as a bright brownish-red gas. The *distinction from bromine* requires, however, that the material, which may be in solution, should be *distilled*, by means of a tubulated flask or small retort, the vapors being condensed in a receiver, and neutralized with an alkali (*c* and *d*). The chromate formed makes a yellow solution (bromine, a colorless solution). As conclusive evidence of chlorine, the chromate (acidified with acetic acid), with lead acetate, forms a yellow precipitate (bromide, a white precipitate, if any):

c. $CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl$

d. $CrO_2Cl_2 + 2(NH_4)OH = (NH_4)_2CrO_4 + 2HCl$

513. The action of *nitric acid* with hydrochloric acid results from the mixture of the two acids, well known as nitro-hydrochloric acid, or "aqua

regia," and used for its free chlorine. Both nitrogen oxy-chloride and nitrogen oxy-dichloride are formed; their relative proportion varying with different conditions:

$$3HCl + HNO_3 = \left\{\begin{matrix} NOCl_2 + Cl \\ or\ NOCl + 2Cl \end{matrix}\right\} + 2H_2O$$

The reaction occurs quite promptly in the concentrated acids without heat, but more rapidly with heat; very slowly in moderately dilute acids, and only to a slight extent if the acids are very dilute.

514. By action of *permanganate*, acidulated with sulphuric acid in warm solution, hydrochloric acid introduced as gas is oxidized to *hypochlorous acid*. Manganese dioxide and sulphuric acid may be used, instead of permanganate, with the same product. In dilute neutral solution, no immediate change occurs between permanganate and chlorides.

515. The *three chlorides insoluble* in water (506) are not transposed or dissolved by acids, except that mercurous chloride is dissolved, by nitric acid and by chlorine, as mercuric salt. They are dissolved for analysis by decomposition with **alkali hydrates** (677). **AgCl** or $PbCl_2$ is dissolved as sodium chloride, after fusion with sodium carbonate on charcoal (*a*), or in a porcelain crucible (*b*):

a. $4AgCl + 2Na_2CO_3 + C = 4Ag + 4NaCl + 3CO_2$

b. $PbCl_2 + Na_2CO_3 = PbO + 2NaCl + CO_2$

516. Heated in a bead of microcosmic salt, previously saturated with copper oxide in the inner blow-pipe flame, chlorides impart a *blue color* to the outer flame, due to copper chloride.

For **Separation of chlorides** from bromides and iodides, see 576 and 577; for separation from chlorates with nitrates, see 581.

CHLORIC ACID.

517. When concentrated, a colorless, syrupy liquid, having a slight odor, resembling nitric acid. It first reddens litmus, and then bleaches it. Chloric acid is somewhat instable at ordinary temperatures; when heated, it rapidly decomposes with formation of yellow products, including perchloric acid ($HClO_4$), chlorine and water. It oxidizes organic and other combustible substances with violent rapidity. For a list of its products as an oxidizing agent, see 823.

518. Chlorates are produced—together with chlorides—by action of chlorine upon bases, according to equation *b*, 501.

All chlorates are resolved by heat into chlorides and oxygen ($HCl + 3O$). In presence of various metallic oxides, etc., the oxygen is separated more easily, the metallic oxides remaining unchanged. With manganese dioxide, the oxygen of potassium chlorate is obtained at about 200° C.; ferric oxide, at 120° C.; platinum, black, at 270°. Copper oxide and lead dioxide may be used. When *triturated or heated* with **combustible substances**, charcoal,

organic substances, sulphur, sulphites, cyanides, thiosulphates, hypophosphites, reduced iron, etc., etc.—*chlorates violently explode*, owing to their sudden decomposition, and the simultaneous oxidation of the combustible material. This explosion is more violent than with corresponding mixtures of nitrates (as in gunpowder, 602).—Potassium chlorate, fused with **PbO**, forms PbO_2; with alkali and **MnO** or MnO_2, *manganate* is formed.

519. All the chlorates are **soluble in water**; those of the first group bases being somewhat unstable in solution. Like nitric and acetic acids, chloric acid is *not precipitated*. Except the mercurous, the least soluble of the metallic chlorates is that of potassium, which requires 12 to 16 parts of cold water for its solution. Potassium chlorate is only slightly soluble in alcohol. Chlorates are usually **identified** by the gaseous products of decomposition (520).

520. Sulphuric acid causes dissociation of chlorates—if in the solid state, with *detonation*, and unless in small quantities, with violent explosion; and with formation of *greenish-yellow gas*, dichlorine tetroxide. Perchlorate is likewise formed. The gas has the odor, oxidizing and bleaching power of chlorine, and it imparts its color to solutions in which it is formed. The products vary with conditions, but are chiefly formed as follows:

$$3KClO_3 + 2H_2SO_4 = 2KHSO_4 + KClO_4 + Cl_2O_4 + H_2O$$
$$2Cl_2O_4 = Cl'''_2O_3 + Cl^{v}{}_2O_5$$

521. If a dilute solution of a chlorate is colored light blue with the solution of indigo in sulphuric acid, and the solution kept cold, no bleaching occurs, even with the further addition of dilute sulphuric acid. But, on addition of solution of sodium sulphite, the color soon disappears, by formation of chlorine or its oxides.

522. Hydrochloric acid decomposes chlorates, rapidly when heated, with the formation of free *chlorine* and dichlorine tetroxide—the mixture called *euchlorine*. The gas and solution have the color, odor, and bleaching effect of chlorine, intensified. This is a ready and effective means of generating chlorine for analytical purposes. The proportion of free chlorine to oxidized chlorine is variable; the subjoined equations showing the character of the results:

$$2KClO_3 + 4HCl = 2KCl + Cl_2O_4 + 2Cl + 2H_2O$$
$$3KClO_3 + 10HCl = 3KCl + Cl_2O_4 + 8Cl + 5H_2O$$
$$4KClO_3 + 16HCl = 4KCl + Cl_2O_4 + 14Cl + 8H_2O$$

For **separation** of chlorates from nitrates, see 580; from nitrates with chlorides, see 581.

523. PERCHLORIC ACID, $HClO_4$, is a colorless liquid, distilling with partial decomposition, forming a crystallizable hydrate, and decomposing by reducing agents with explosion. It is obtained by distillation of perchlorates with sulphuric acid. Hydrochloric and nitric acids do not decompose perchlorates in water solution. All the metallic perchlorates are soluble in water; **potassium** perchlorate requiring 58 parts (rubidium perchlorate, 92 parts) of water at 21° C.; the other metals forming salts more freely soluble. The potassium salt is insoluble in alcohol. In *ignition*, perchlorates act very much like chlorates, but more explosively.

HYPOCHLOROUS ACID.

524. Hypochlorous *anhydride*, Cl_2O, can be obtained at –20° C. (–4° F.), by the reaction, $HgO + 4Cl = Cl_2O + HgCl_2$, as an orange-colored, explosive liquid, gaseous at ordinary temperatures, and decomposing, spontaneously and sometimes violently, into chlorine and oxygen. It dissolves in water, forming hypochlorous acid, $HClO$.

Hypochlorous acid, in aqueous solution, is a yellow liquid; when strong, decomposing rapidly at 0° C. (32° F.); when dilute, decomposing gradually by boiling (*a*); decomposed by hydrochloric acid (*b*), and by metals (*c*)—its decompositions furnishing chlorine or oxygen, or both chlorine and oxygen.

a. $2HClO = H_2O + 2Cl + O$

b. $HClO + HCl = H_2O + 2Cl$

c. $2HClO + 2Zn = ZnO + ZnCl_2 + H_2O$

$2HClO + 2Ag = 2AgCl + H_2O + O$

525. The **Hypochlorites** *are formed* by treating bases with chlorine (short of saturation), as shown in *b*, 501. The calcium hypochlorite and chloride, mixed or combined together as formed by action of chlorine upon calcium hydrate, is in very extensive use—as chlorinated lime, or "chloride of lime" [$CaCl_2 + Ca(ClO)_2$, *or* $2Ca(OCl)Cl$]. The sodium hypochlorite-and-chloride—mixed as formed by chlorine in solution of sodium hydrate or sodium carbonate, or by double decomposition between solution of the calcium hypochlorite-and-chloride and solution of sodium carbonate—is pharmacopœial, under the name of solution of chlorinated soda ($NaCl.NaClO$). The chemical structure of these important chlorinated compounds has been difficult to ascertain.

526. Hypochlorites are very *instable*, whether solid or in solution, decomposing by the weakest acids, by the carbonic acid of the air (*a*), and by heat (*b*), also to some extent at ordinary temperatures. In this manner, they act as *powerful oxidizing agents*. The deportment of hypochlorites is represented by the action of *chlorine in alkali solutions* (501 *b*); a convenient agent of especial force, as for the decomposition of ammonia (63 *b*).

a. A. $Ca(ClO)_2 + CO_2 = CaCO_3 + 2Cl + O$

B. $CaCl_2.Ca(ClO)_2 + 2CO_2 = 2CaCO_3 + 4Cl$

C. $Ca(ClO)_2.CaCl_2 + 2H_2SO_4 = 2CaSO_4 + 2H_2O + 4Cl$

D. $2NaClO + 2HCl = 2NaCl + H_2O + 2Cl + O$

b. In boiling solutions: $3Ca(ClO)_2 = Ca(ClO_3)_2 + 2CaCl_2$

At a higher temperature: $Ca(ClO_3)_2 = CaCl_2 + 6O$

527. All hypochlorites are **soluble in water**; those of the first group metals being especially instable. Their solutions bleach **litmus** and indigo.

528. **Silver nitrate**, added to the solutions of hypochlorites with chlorides, precipitates the chloride, **AgCl**, at first leaving hypochlorites in solution;

while the soluble *silver hypochlorite* quite rapidly decomposes with the precipitation of chloride and formation of chlorate of silver (*a*), the latter slowly changing to chloride (518):

a. $3AgClO = 2AgCl + AgClO_3$ (corresponding to *b*, 526)

529. BROMINE, at ordinary temperatures, is a brown-red, intensely caustic liquid, freely evolving brown-red, corrosive vapors of a suffocating, chlorine-like odor, and boiling at 47° C. (117° F.) It is **soluble** in 33 parts of water, with an orange-yellow color; and freely soluble in alcohol, ether, chloroform, and in **carbon disulphide**—with the same or a deeper color. Carbon disulphide, and chloroform, after agitation with its dilute water solutions, remove the bromine as a subsiding liquid in a yellow to red-brown layer; ether, less perfectly, in a supernatant layer of the same color. It dissolves colorless **in alkali hydrates,** with combination, forming bromides and bromates. The change corresponds exactly to that of chlorine, as shown in equation *b*, 501. It dissolves, without combination or loss of color, in solutions of hydrobromic acid, and of bromides.

530. In vapor or solution, bromine bleaches **litmus** and indigo; colors **starch-paste** yellow; precipitates **silver** salts, yellow-white, bromide and bromate (as by equation *c*, 501); and lead salts, white. Bromine decomposes **hydrosulphuric acid** with separation of sulphur, and subsequent production of **sulphuric acid**; changes ferrous to ferric salts, and (in presence of water) acts as a strong oxidizing agent. It displaces iodine from iodides, and is displaced from bromides by chlorine; its character being intermediate between that of chlorine and that of iodine (820 *i*). For Oxidations by bromine, see 824.

531. The **Acids of Bromine** are:

Hydrobromic acid, HBr'.
Bromic acid, $HBr^{V}O_3$.
Hypobromous acid, $HBr'O$.

HYDROBROMIC ACID.

532. Absolute hydrobromic acid is gaseous at ordinary temperatures, but dissolves freely in water. The strong solution gives off gas in the air more rapidly than aqueous hydrochloric acid, and boils below 100° C.; the dilute solution boils above 100 C., and if very dilute is concentrated by boiling. In gaseous state or in solution, hydrobromic acid is *colorless;* but it is slowly decomposed by atmospheric air [$2HBr + O = H_2O + 2Br$] with the presentation of the color of free bromine; the solution deepening in yellow-brown tint, as bromine is displaced by oxygen, and dissolved by the hydrobromic acid.

Neither hydrobromic acid nor a metallic bromide will give the yellow color to **starch paste.**

533. Hydrobromic acid is produced from *the metallic bromides*, by transposition with **dilute sulphuric acid:**

$$2KBr + H_2SO_4 = K_2SO_4 + 2HBr$$

But the bromides of mercury, silver, lead, and tin, are transposed by sulphuric acid with difficulty, or not at all (compare chlorides, 505).

534. **The Bromides** (including hydrogen bromide) are decomposed by **oxidizing agents**, with *liberation of bromine.* Thus: by **chlorine** (820 *b*) (not by iodine); by bromic acid (*a*); by **nitric acid** (814 *g*); by strong and hot **sulphuric acid** (819 *b*); and, in hot solution, acidulated, by **manganese dioxide** (*b*). Further, see 835.

a. $5KBr + KBrO_3 + 3H_2SO_4 = 3K_2SO_4 + 3H_2O + 6Br$

b. $2KBr + 2H_2SO_4 + MnO_2 = K_2SO_4 + MnSO_4 + 2H_2O + 2Br$

535. The **solubilities** of the bromides lie intermediate between those of the chlorides and those of the iodides, not differing much from the former. In general terms, all *bromides are soluble in water, except those of the first group bases.* Further, mercuric bromide is only sparingly soluble in water. Lead bromide is less soluble than lead chloride. Bismuth bromide is decomposed by water, to a greater extent than bismuth chloride (295), and antimonious bromide is decomposed by water. Cuprous bromide is formed as a precipitate by reduction from the soluble cupric bromide.

The *double bromides* of lead and potassium or sodium, and of silver and potassium or sodium, are soluble in a little water containing alkali bromides as concentrated solutions, but are decomposed by much water; the potassio and the sodio mercurous and mercuric bromides are soluble in water.

In *alcohol*, the alkali bromides are sparingly or slightly soluble; calcium bromide, soluble; mercuric bromide, soluble; mercurous bromide, insoluble.

Silver bromide is sparingly soluble in *ammonium hydrate;* nearly insoluble in ammonium carbonate solution.

In **analysis**, bromides are usually identified by the color of a carbon-disulphide solution of free bromine, iodine, if present, being first removed (539, 576).

536. **Silver nitrate** solution precipitates, from solutions of bromides, *silver bromide*, **AgBr**, yellowish-white in the light, slowly becoming gray to black. The precipitate is insoluble in dilute nitric acid, sparingly soluble in concentrated aqueous ammonia, nearly insoluble in concentrated solution of ammonium carbonate, slightly soluble in excess of alkali bromides, soluble in solutions of alkali cyanides and thiosulphates. It is decomposed by chlorine.

537. Solution of **mercurous nitrate** precipitates *mercurous bromide*, Hg_2Br_2, yellowish-white, soluble in excess of alkali bromides.

538. Solutions of **lead salts** precipitate, from solutions not very dilute, *lead bromide*, $PbBr_2$, white (314 and 535).

539. **Sulphuric acid** decomposes bromides: when dilute, mostly with production of hydrobromic acid (533); when concentrated, chiefly with forma-

tion of **bromine.** The vapor from the hot mixture reddens or bleaches *litmus;* has the yellowish-brown *color* and suffocating *odor* of bromine, and when cooled colors **starch-paste** yellow.

Chlorine Water separates the bromine much more quickly and completely, giving better results in dilute solutions, but in excess it decolors the bromized starch.

The more delicate test is made by adding **carbon disulphide,*** then dilute chlorine water, drop by drop, in the cold solution, then agitating, and allowing the heavier liquid to subside (529). The presence of bromine is indicated by a *yellow* color, or if there is much bromine a yellowish-brown to brownish-red color. Iodine colors violet. *If free iodine is present,* bromine cannot be identified, by its vapor, its color with starch, or its color in solution with carbon disulphide. All the iodine of iodides will be liberated before any of the bromine can be: therefore, before these tests can be made for bromine, the iodine must either be oxidized to iodic acid, or wholly expelled, as directed in 576.

Dilute hydrochloric acid will not color dilute solutions of bromides, or yield much color to disulphide of carbon; *in absence of oxidizing agents.*

540. For **Separation** of bromides from iodides and chlorides, see 576; from bromates, 546 and thereafter.

541. Bromides of potassium, sodium, and of most other metals, are not decomposed by **ignition.** Silver bromide melts undecomposed; but is slowly reduced, and blackened, in the air and by light.

Tested in the cupric bead, according to 516, bromides give a greenish-blue color to the outer flame—not very marked.

BROMIC ACID.

542. In concentrated aqueous solution, a colorless, acrid, and instable liquid. At 100° C., it is decomposed into hydrobromic acid and oxygen.

It is rapidly decomposed by all **reducing agents,** as given in detail in 826.

543. Bromates are produced together with bromides by the action of bromine upon bases; the reaction being expressed by equation *b,* 501, substituting **Br** for **Cl.**

544. By ignition, bromates are reduced to bromides (in case of **K, Na, Ag, Hg**), like chlorates in the same condition. Other bromates change to oxides, as follows:

$$Zn(BrO_3)_2 = ZnO + 5O + 2Br$$

545. By **reducing agents,** bromates are mostly decomposed in the same manner as bromic acid (542). Mixed with sulphur, carbon, and other combustible substances, they furnish oxygen and cause **explosion,** like the chlorates (518).

* *Carbon disulphide* is a better color-solvent, for bromine or iodine, than chloroform, and far better than ether. It must be free from sulphurous or sulphuric acids. Saturated chlorine water is liable to act on carbon disulphide, giving it a yellow color, simulating bromine. On adding alcohol to this yellow liquid sulphur precipitates. Hence the direction to use dilute chlorine water, and avoid excess.

546. All the bromates are **soluble in water**; those of the first group bases, but sparingly soluble. **Silver nitrate** precipitates, in solutions not very dilute, *silver bromate*, $AgBrO_3$, white, very sparingly soluble in water, soluble in ammonium hydrate, not easily soluble by nitric acid; its color and solubility in ammonium hydrate differing a little from the bromide (536). It is decomposed by hydrochloric acid with evolution of bromine —a distinction from bromides and from other argentic precipitates.

547. Sulphuric, hydrochloric, and nitric acids, liberate bromic acid from metallic bromates. With very **dilute sulphuric acid**, in cold dilute solution of pure bromate, very little bromine is set free—the $HBrO_3$ mostly remaining for some time intact, and the solution colorless; so that carbon disulphide will not extract much color. The gradual decomposition of the $HBrO_3$ is first a resolution into **HBr** and **O**; and as fast as **HBr** is formed, it acts with $HBrO_3$, so as to liberate the bromine of both acids. Now, if the solution contained bromide as well as bromate, an abundance of free bromine is obtained *immediately* upon the addition of dilute sulphuric acid in the cold (equation *a*, 534).

548. Hence, if dilute sulphuric acid in the dilute cold solution does not color the carbon disulphide, and if the addition of solution of pure potassium **bromide** immediately develops the yellow color, while it is found that no other oxidizing agent is present, we have corroborative evidence of the presence of a bromate. And, if we treat a solution known to contain bromide with dilute sulphuric acid and carbon disulphide, and obtain no color, we have conclusive evidence of the *absence* of bromates.

549. A mixture of *bromate and iodate*, treated with **hydrochloric acid**, furnishes bromine without iodine, coloring carbon disulphide yellow.

550. The ignited residue of bromates (544), in all cases if the ignition be done with sodium carbonate, will give the tests for bromides.

551. IODINE is solid; in soft scales or hexagonal prisms, with a dark iron-gray color and graphitoidal lustre. It is precipitated as a brownish-black powder. It vaporizes very slightly at ordinary temperatures—with a characteristic odor, resembling chlorine, but more offensive. It melts at 107° C. (224° F.), and boils at 180° C. (356° F.); the vapor having an intense, bright violet color.

552. It is slightly **soluble** in water, dissolving in 7,000 parts; freely soluble in alcohol, ether, chloroform, carbon disulphide, petroleum naphtha, glycerine, and in solutions of iodides (including **HI**). All solutions of uncombined iodine have red-brown, brownish-yellow, or violet tints. *The carbon disulphide solution is violet* (marked distinction from bromine), the other solutions brownish-yellow (but little darker than those of bromine). Solutions by chemical combination are referred to in 554.

553. Starch-paste is colored blue by a little iodine, violet by a further addition of iodine; and by still greater excess a blue green (or, in presence of bromine, a brown) color is produced. This test is exceedingly delicate for iodine.*

* *The union of iodine and starch* is probably an example of molecular adhesion rather than of union within molecules. When dry starch is saturated with ether solution of iodine, and exposed for some time to the heat the water-bath, about 4 per cent. of iodine is retained. This corresponds nearly with the formula $(C_6H_{10}O_5)_{20}I$. Prepared under other conditions, it holds 7 to 8 per cent. of iodine $(C_6H_{10}O_5)_{10}I$.

The iodized starch is discolored by heating in solution, to 70° or 80° C. (158° to 176° F.), but regains its color on cooling. Its color is destroyed by strong chlorine, and by alkalies.

No compound of iodine colors starch.

554. Though expelled from combination with bases by chlorine, bromine, nascent oxygen, and other strong electro-negatives (557), iodine acts in many relations as *an oxidizing agent*, readily entering into combination, as iodides, when acted on by reducing agents. On the other hand, in relation to a limited number of active electro-negatives, it may act as *a reducing agent*, becoming the subject of oxidation, in the formation of iodates (557). Iodine chlorides also are formed, ICl_5, ICl_3, and **ICl**, of yellow to brown colors.

Iodine slowly bleaches litmus and other vegetable colors, and stains the skin yellow-brown.

Colorless solutions are formed by all the alkali hydrates with iodine; the fixed alkali hydrate forming iodides and iodates (*a*). With **ammonia** in water solution, it dissolves more slowly, becoming colorless; the solution contains the most of the iodine as ammonium iodide, and liable to deposit a dark-brown powder, termed "*iodide of nitrogen*," very easily and violently *explosive* when dry. This substance is a variable substitution of one, two, or three atoms of **I** for **H** in NH_3 (63 *c*). Among **reducing agents**, solutions of **thiosulphates** quickly dissolve and decolor iodine, forming iodides and a more highly oxidized acid of sulphur, tetrathionic acid (*b*). Solutions of sulphites and of sulphurous acid convert iodine into colorless hydriodic acid (*c*).—**Arsenious acid** is oxidized to arsenic acid by action of iodine, which becomes colorless as hydriodic acid (*d*). Hydrosulphuric acid dissolves iodine as hydriodic acid, the solution of which is so prepared (*e*). *The alkali hydrates, and reducing agents, decolor iodized starch*, by taking its free iodine into combination. Further, see 827.

a. $6I + 6KOH = 5KI + KIO_3 + 3H_2O$ (corresponding with 501 *b*).

b. $I + Na_2S_2O_3 = NaI + NaS_2O_3$ (compare *c*).

c. $2I + H_2O + Na_2SO_3 = 2HI + Na_2SO_4$

d. $2I + H_2O + H_3AsO_3 = 2HI + H_3AsO_4$

e. $2I + H_2S = 2HI + S$

The chief **Acids of Iodine** are:

Hydriodic acid, HI'.

Iodic acid, $HI^{V}O_3$ (or $H_2I_2O_6$).

Periodic acid, $HI^{VII}O_4$.

HYDRIODIC ACID.

555. Absolute hydriodic acid is **gaseous** at ordinary temperatures, but freely **soluble** in water; being easily obtained in **solution** containing 50 to 60 per cent. of acid, and having a boiling point above that of water, but giving off some vapor at common temperatures. Both the gas and the solution are colorless, and redden litmus. Hydriodic acid *decomposes* gradually in the air with

separation of iodine—more rapidly at higher temperatures; so that the evolved gas is always strongly colored with iodine, and the exposed solution commences at once to turn brownish-yellow with the free iodine dissolved by the acid. The liberated gas has a slight chlorine-like odor, and a stronger *offensive odor* (due to both the iodine and hydriodic acid). Upon brief exposure, both the gas and the solution give abundantly the reactions of free iodine (with starch, carbon disulphide, etc.)

556. Like hydrochloric and hydrobromic acids, *hydriodic acid is produced by transposition from the metallic iodides*, by the action of **dilute sulphuric acid** (see 533). Also, by large excess of **hydrochloric** and **hydrobromic** acids. The iodides of silver, lead, mercury, and tin, are transposed with difficulty by sulphuric acid, more readily by hydrochloric acid.

557. The **iodides** (including hydrogen iodide) are decomposed by **oxidizing agents** more readily than the bromides. At first, by oxidation of the base, *iodine is set free;* after which some of the more active electro-negatives oxidize iodine to *iodates.*

Ozone promptly decomposes all iodides, not excepting those of the alkali metals; while atmospheric oxygen decomposes hydriodic acid and iron and calcium iodides but slowly, and alkali iodides not at all. *Iodine* is liberated from iodides at once by **chlorine, bromine** (*a*), **iodic acid** (*b*), and bromic acid. Iodine is first set free and then oxidized to *iodic acid*, by **acidulated chlorate**, by **hypochlorites** (with occurrence of iodine chlorides and final formation of periodates), and by concentrated **nitric acid** with heat (*c*); dilute nitric acid slowly separating iodine (*d*), and scarcely decomposing lead, silver, and mercury iodides. Acidulated **potassium nitrite** acts more promptly than nitric acid. **Manganese dioxide** with sulphuric acid is employed in the manufacture of iodine (*e*). **Permanganate** solution, added in excess, produces *iodates*, iodine being first separated and at last all oxidized; in neutral or alkaline dilute solutions (1 part salt to 240 parts water), a distinction from bromides, which do not decolor the permanganate. **Chromates**, acidulated, cause immediate separation of iodine. **Concentrated sulphuric acid** (*f*) and **ferric chloride** (*g*) are reduced by iodides. Further, see 828.

a. $HI + Br = HBr + I$

b. $5KI + KIO_3 + 3H_2SO_4 = 3K_2SO_4 + 3H_2O + 6I$

c. $KI + 2HNO_3 = KIO_3 + 2NO + H_2O$

d. $3KI + 4HNO_3 = 3KNO_3 + NO + 2H_2O + 3I$

e. $2KI + 2H_2SO_4 + MnO_2 = K_2SO_4 + MnSO_4 + 2H_2O + 2I$

f. $2HI + H_2SO_4 = 2H_2O + SO_2 + 2I$

g. $2KI + Fe_2Cl_6 = 2FeCl_2 + 2KCl + 2I$

558. The metallic iodides are all **soluble in water**; *except* those of **Ag, Pb,** and **Hg**, except palladious iodide, cuprous iodide, bismuth iodide decomposed by water, and stannous iodide sparingly soluble in water. Lead iodide is sparingly soluble, and mercuric iodide very sparingly soluble in water.

The *double iodides* of lead, silver, and mercury with alkali metals—as **KI.AgI**, and $(KI)_2HgI_2$—are soluble in water; *i.e.*, the *iodides of first group metals* are soluble in solutions of alkali iodides, by combination; mercurous iodide in part only, as explained in 352.

Alcohol dissolves many of the iodides soluble in water—including the alkali iodides, and those of barium and calcium—and dissolves mercuric, but not mercurous or argentic, iodide.

Silver iodide is but very sparingly soluble in concentrated solution of ammonium hydrate, and insoluble in hot solution of ammonium acid carbonate (distinctions from the chloride). It dissolves in solution of potassium cyanide.

The iodides of silver and of lead are soluble by decomposition in solution of alkali thiosulphates (*a*); lead iodide in fixed alkalies (309). The iodides of silver and mercury are not decomposed, the iodide of lead slowly decomposed, by dilute nitric acid.

a. $AgI + Na_2S_2O_3 = NaI + NaAgS_2O_3$

In **analysis,** iodides are most easily identified by the color of the carbon disulphide solution of liberated iodine (565). The silver precipitate of iodide is separable from chloride by solution of the latter in ammonium hydrate (577).

559. Silver nitrate solution in excess precipitates, from solutions of iodides, *silver iodide*, **AgI**, yellow-white, blackening in the light (without notable separation of iodine). For the solubilities of the precipitate, see 558, and compare 333. For its separation from chloride and bromide, see further, 577.

560. Solution of mercuric chloride precipitates the bright, yellowish-red to red, *mercuric iodide*, HgI_2. The precipitate redissolves on stirring, after slight additions of the mercuric salt, until equivalent proportions are reached, when its color deepens. For the solubilities of the precipitate, see 360.—Solution of mercurous nitrate precipitates mercurous iodide, Hg_2I_2, yellow to green (see 352).

561. Solution of **plumbic nitrate** or acetate precipitates, from solutions of iodides not very dilute, *lead iodide*, PbI_2, bright-yellow—soluble, as stated in full in 315.

562. Palladious chloride, $PdCl_2$, precipitates, from solutions of iodides, *palladious iodide*, PdI_2, black, insoluble in water, alcohol, or dilute acids, and visible in 500,000 parts of solution. The reagent *does not precipitate bromine* at all in moderately dilute solutions, slightly acidulated with **HCl**. Palladious iodide is slightly soluble in excess of the alkali iodides, and is soluble in ammonium hydrate (486).

563. Copper sulphate, with sulphurous acid or other reducing agent, precipitates from solutions of iodides, the *cuprous iodide*, Cu_2I_2, which is

white, if there is sufficient reducing agent to prevent the precipitation of iodine, brown. The precipitate is not altogether insoluble in water; therefore the filtrate responds to the delicate tests for iodine (*equation in* 279 *b*). *Bromine is not precipitated* with copper.

564. **Concentrated sulphuric acid** decomposes iodides, solid or in concentrated solution, with the reaction stated at 557 *f*. The evolved *gas* has the violet color of iodine, and the offensive odor of mingled iodine and hydriodic and sulphurous acids. When cooled and somewhat diluted, the *liquid* gives the iodine color with **starch** (553); or, on agitating gently with carbon disulphide, and permitting the latter to subside, the beautiful *violet tint* of iodine in this solvent.

565. **Chlorine water** separates iodine more satisfactorily, in this test with carbon disulphide, especially from dilute solutions. The chlorine-water should be dilute and added (after the starch-paste or carbon disulphide) drop by drop; as an excess will destroy all characteristics of free iodine by formation of iodine chlorides and iodic acid (576).

Nitrous acid—as from zinc and nitric acid or from acidulation of nitrites—is a good agent to displace iodine. It should be very sparingly used (607). **Bromine** water is also employed for the same purpose.

Bromides do not interfere with the easy recognition of free iodine; unless an excess of chlorine is added, no bromine will be liberated; and if liberated, it does not modify the color of iodine, in starch or in carbon disulphide, unless the bromine is in much greater quantity, and even then the color represents iodine.

566. Solution of ferric chloride, added in the proportion of 6 or 8 drops to 3 or 4 cub. cent. (a fluid drachm or a little less) of the solution tested, together with carbon disulphide, slowly develops the violet tint in the subsiding liquid, if iodine is present (557 *g*)—a distinction from bromine.

567. For **Separation** of iodides from chlorides and bromides, 576; from iodates, 573.

568. The iodides of the alkali metals and of the first group metals fuse without decomposition; those of mercury sublime undecomposed; but other non-alkali iodides are mostly decomposed by ignition.

Treated in the cupric bead of microcosmic salt, as directed for chlorine in 516, iodides give an emerald *green* glass.

IODIC ACID.

569. Absolute iodic acid, HIO_3 (or $H_2I_2O_6$), is a white, crystallizable, odorless solid, *permanent* in the air; at 170° C. (338° F.) resolved into water and iodic anhydride (H_2O and I_2O_5). Iodic anhydride is a crystallizable solid, at high temperatures resolved into iodine and oxygen. Bromic anhydride is not known. Iodic acid is freely soluble in water and in alcohol; the solutions reddening litmus, and afterwards bleaching it.

570. Iodic acid is formed by prolonged action of nitric acid and other oxidizing agents upon iodine. Its salts, the iodates, are formed together with iodides in dissolving

iodine in aqueous alkalies (554 *a*), as well as by oxidation of iodides (557). Iodic acid is easily obtained by transposing metallic iodates with sulphuric acid (*a*); its radical not easily breaking up when separated from metals, as chloric and bromic acids do.

a. $2KIO_3 + H_2SO_4 = K_2SO_4 + 2HIO_3$.

571. The Iodates—including hydrogen iodate—are decomposed by **reducing agents**, with the formation of iodides (of metals or of hydrogen) and with other results.

Sulphurous acid is oxidized from iodic acid, first with separation of *iodine* (*a*); then, by excess of the sulphurous acid, with formation of *hydriodic acid* (*b*). Hence, sulphurous acid, added *short of saturation*, **with starch**, forms a delicate test for iodates, and a distinction from iodides; but excess of the reagent destroys the color. **Thiosulphates** produce iodine, or hydriodic acid. **Hydrosulphuric acid** also reduces iodates, precipitating at first iodine and sulphur (*c*). With excess of the reducing agent, the final products are hydriodic acid and sulphur (*d*); with excess of the iodate, iodine and sulphate (*e*). **Hydriodic acid** instantly separates, from iodic acid, all the iodine of both acids (*f*); hence, an intermixture of a metallic iodate with an iodide is revealed at once by adding a dilute or weak acid that will not itself liberate iodine, but will produce both the acids of iodine, so that they can decompose each other. In solution of potassium iodide, for example, a slight addition of **tartaric acid** shows the presence of iodate by the *immediate*, not progressive, appearance of the iodine color, the test being more delicate by use of carbon disulphide. In solutions not of iodides, **an iodide** may be added, with tartaric or **acetic acid**, in search for iodates. But it must be remembered that pure iodides, so treated, form hydriodic acid, which, by atmospheric oxidation, *progressively* liberates iodine, and will soon give a deep color to starch or carbon disulphide. **Hydrochloric acid** forms with iodates mostly iodine chlorides (*g*), iodine not being liberated (distinction from bromates, 549). **Morphia** reduces iodic acid, with separation of iodine as a final product. Further, see 829.

a. $2KIO_3 + 5H_2SO_3 = 2I + 2KHSO_4 + 3H_2SO_4 + H_2O$

Or: $2HIO_3 + 5H_2SO_3 = 2I + 5H_2SO_4 + H_2O$

b. The iodine is taken up by excess of H_2SO_3, as in 554 *c*.

c. $2HIO_3 + 5H_2S = 2I + 6H_2O + 5S$

d. $HIO_3 + 3H_2S = HI + 3H_2O + 3S$

e. $8KIO_3 + 5H_2S = 8I + 3K_2SO_4 + 2KHSO_4 + 4H_2O$

f. $HIO_3 + 5HI = 6I + 3H_2O$ (For acidulated salts, see 534 *b*).

g. $KIO_3 + 6HCl = (ICl_3 + 2Cl) + KCl + 3H_2O$

Iodates *in dry mixture* with combustible bodies are reduced, on heating or concussion, with *detonation*, but much less violently than chlorates or nitrates. Heated alone, iodates are either reduced to iodides with liberation of oxygen (iodates of potassium, sodium); or to oxides with liberation of iodine and oxygen (iodate of barium). Compare Bromates, 544.

572. The iodates are either **insoluble or sparingly soluble in water, except** those of the alkali bases, a marked difference from bromates and chlorates. Barium, silver, and lead iodates are insoluble in water. The alkali metals form acid iodates. In alcohol most of the iodates are insoluble; barium iodate, insoluble; calcium and potassium iodates, scarcely at all soluble (distinctions from iodides).

Silver iodate is readily soluble in **ammonium hydrate** (distinction from iodide); it is slightly soluble in dilute nitric acid (more so than the iodide).

Iodates are **identified** by separation of free iodine, known by its color in carbon disulphide solution or in mixture with starch (571); and by precipitation of barium salt (572).

573. Solution of **silver nitrate** precipitates, from even very dilute solutions of iodates and from solutions of iodic acid if not very dilute, *silver iodate*, $AgIO_3$, white, crystalline, soluble in ammonium hydrate. *In the ammonia solution*, **hydrosulphuric acid** precipitates *silver iodide*.

Barium chloride precipitates *barium iodate*, $Ba(IO_3)_2$, nearly insoluble in cold and little soluble in hot water, insoluble in alcohol, scarcely soluble in dilute nitric acid, readily soluble in dilute hydrochloric acid. Hence, dilute solutions of free iodic acid should either be neutralized or tested with barium nitrate. This precipitate, by addition of alcohol, is a complete *separation from iodides*, and, when well washed, decomposed with a very little sulphurous acid (571 *a*), and found to color carbon disulphide violet, its evidence for iodic acid is conclusive. Barium iodate is transposed with ammonium carbonate, on digestion in solution and with ammonium hydrate (separation from periodate).

Salts of **lead** give a white precipitate of *lead iodate*, $Pb(IO_3)_2$. Ferric chloride gives, in solutions not dilute, a yellowish-white precipitate of *ferric iodate*, $Fe_2(IO_3)_6$, sparingly soluble in water, and freely *soluble in excess of the reagent*. Boiling decomposes it.

Alcohol precipitates *potassium iodate* from water solution, an approximate separation from iodide.

574. Comparison of Certain Reactions of the Acids of Chlorine, Bromine, and Iodine,

Taken in Water Solution, as Potassium Salts, or other Soluble Compounds.

	Chlorides.	Bromides.	Iodides.	Chlorates.	Iodates.	Hypochlorites.
$AgNO_3$, in excess, ...	**AgCl**, white (508).	**AgBr**, white (536).	**AgI**, yellow-white (559).	No pre (519).	$AgIO_3$, white (572).	No pre. (528).
$AgNO_3$, with excess of the solution tested.	Pre.? (328).	Pre. (333).	Sol. (333).	. . . . .	Pre.	
NH_4OH, to the Ag pre. . . .	Dissolved.	In part dissolved.	Not dissolved.	. . . . .	Dissolved.	
$HgCl_2$, in excess, ...	. . . . .	No pre.	HgI_2, yellow-red.	No pre.	$Hg(IO_3)_2$.	No pre.
$HgCl_2$, with excess of the solution tested.	. . . . .	No pre.	No pre. (360).	. . . . .	Pre.	
$Hg_2(NO_3)_2$, in excess, . . .	Hg_2Cl_2, white.	Hg_2Br_2, white.	Hg_2I_2 (352).	No pre.	Pre.	No pre.
$BaCl_2$, ...	. . . . .	. . . . .	. . . . .	. . . . .	$Ba(IO_3)_2$ (573).	
$CuSO_4$, with H_2SO_3, ...	. . . . .	. . . . .	Cu_2I_2 (563).	. . . . .	(571 *a*).	
H_2SO_4, dilute, ...	**HCl** (soluble gas).	**HBr**	**HI** (556).	$HClO_3$, Cl_2O_4, **Cl**	HIO_3 (570).	**Cl** (bleaches).
HCl, ...	. . . . .	**HBr**	**HI**	Cl_2O_4 and **Cl**	. . . . .	**Cl**
Cl, ...	. . . . .	**Br** (539).	**I** (565).			
Chromate, with H_2SO_4, . . .	CrO_2Cl_2 (512).	**Br**	**I**			
$KMnO_4$, dilute, neutral, . .	. . . . .	. . . . .	**I** (557).			
Na_2SO_3, with H_2SO_4, . . .	. . . . .	. . . . .	. . . . .	Chlorides.	**I** and **HI** (571).	**HCl**
H_2S, ...	. . . . .	. . . . .	. . . . .	**S**, H_2SO_4 (817 *f*)	**I**, **HI**, **S** (571).	**S**, H_2SO_4.

575. THE SEPARATION of the acids of **chlorine, bromine, and iodine** is effected by oxidations, reductions, color solutions, precipitations, separative solutions, and vaporizations. In many cases of separation, the acids to be separated will act upon each other.

576. The **Recognition** of chlorides, bromides, and iodides—by evolving their chlorine, bromine, and iodine, *in presence of each other*—can be accomplished as follows—for the iodine the test being very easy; for chlorine, indirect, but unmistakable; for bromine, dependent upon much care and discretion.*

The **Iodine** is liberated with dilute **chlorine-water,** added drop by drop, and is readily detected by **starch, or carbon disulphide,** according to 565. (As to interference of sulphocyanates, see 643.) The **Chlorine** is vaporized (from another portion) as *chlorochromic anhydride,* and the latter identified by its color and its various products, as described in 512. Before the **Bromine** is identified the iodine is to be either *removed as free iodine, or oxidized to iodate* (539). The oxidation to iodic acid is effected as follows: Treat with good chlorine water till free iodine no longer shows its color; add a drop or two more of the chlorine water, and dilute with water, keeping cool; then add the carbon disulphide, agitate, and leave the solvent to settle, for the yellow color of bromine. The removal of free iodine may be done as follows: Add chlorine water, drop by drop, as long as the iodine tint seems to deepen by the addition; add the carbon disulphide, agitate, leave to subside, and remove the lower layer, either by taking it out with a pipette, or by filtration through a wet filter. Repeat, if need be, till iodine color is no longer obtained; then continue, with dilute chlorine water, in test for bromine.

If iodide in large proportion is to be removed, it is well, first, to precipitate it out, as far as possible, by copper sulphate and a reducing agent, as directed in 578. The filtrate is then to be treated by either method above given.

577. The **Separation** by **ammonium hydrate,** *as a solvent of the silver precipitates*—**AgCl, AgBr, AgI**—when conducted with dilute ammonium hydrate, may be made nearly complete between the chloride and the iodide, but it is very imperfect between the bromide and either of the others. The hot and strong solution of ammonium acid carbonate separates the chloride from the bromide (compare 509, 536, 558).

578. The direct *removal of* **iodides** *by precipitation, leaving bromides and chlorides in solution,* can be effected (approximately) by **copper sulphate with sulphurous acid** (563), or quite completely, by **palladious chloride** (562). With the copper sulphate, the

* In consequence of the relative commercial values of bromine and iodine, and the medicinal relations of bromides and iodides, it is of great importance to search commercial iodides for intentional and considerable mixtures of bromides—an impurity likely to escape cursory chemical examination. There are, however, very *slight* and usually unobjectionable proportions of bromides generally to be found in the iodides of commerce, and occurring from the difficulty of exact separation in the manufacture of iodine from kelp.

reduction ought to be thorough; and this result is better secured by sulphurous acid than by ferrous sulphate, and without loading the solution with another metallic salt. The action of palladium chloride is subject to no objection, except the scarcity and expensiveness of the reagent.

579. Chloric acid is separated from *hydrochloric and all other acids of chlorine, bromine, and iodine* (except from hypochlorous acid, and from traces of bromic acid), by remaining in solution during the precipitation by **silver nitrate** (519).

580. Chloric acid is separated *from nitric acid*—after finding that *silver nitrate gives no precipitate* in another portion of the solution, acidulated—by evaporating and igniting the residue, then dissolving, and testing one portion of the solution by **silver nitrate** for the *chloride* formed from chlorate during ignition (518). The other portion of the solution is tested for nitric or nitrous acid.

581. If we have to separate chloric acid *both from nitric and hydrochloric acids,* a solution of **silver sulphate** must be used instead of the nitrate, to precipitate out all the hydrochloric acid. The filtrate from this is evaporated, **ignited,** dissolved and tested, as in 580, for chloride, indicating chlorate in the original solution, and another portion is tested for nitric acid. Also, chlorates are *distinguished* (not separated) *from nitrates,* by oxidation of **ferrous sulphate** in solution with **acetic acid** on heating, and the consequent formation of the *red solution of ferric acetate* (190, 753). The solution tested must contain no free acids, and no nitrites or other oxidizing agents beside the two in question, but may contain chlorides; and, of course, the ferrous sulphate must be pure enough not to color when heated alone with the acetic acid. Mix the ferrous sulphate solution with the acetic acid, boil, then add the solution to be tested, and heat nearly to boiling, for some minutes. If no red color appears, chlorates are absent, and nitrates may be present.

582. **Hypochlorites** are separated *with chlorates* from chlorides (bromides), etc., by **silver nitrate**; and distinguished *from chlorates* (in the filtrate from **AgCl**, etc.), by bleaching litmus, and by their much more rapid decomposition and consequent precipitation of any silver in solution (528). They are also more active than chlorates, as oxidizing agents (526).

583. The identification of **iodic acid** is simple and certain, by use of **reducing agents** (571), or precipitants (573). The identification of **bromic acid**, in presence of other acids, is indicated in 546 to 550.

584. **NITROGEN** is a colorless, odorless, insoluble **gas**; not combining with oxygen or other elements, in their ordinary state, at any temperature. It exists combined with **hydrogen** in the basic anhydride, **Ammonia**, NH_3; with **oxygen** in the radicals of **Nitric acid**, HNO_3, and **Nitrous acid**, HNO_2; and with **carbon** in cyanogen, **NC** or **Cy**, the radical of hydrocyanic and other **Cyanogen acids**. It also forms, with carbon, hydrogen, and oxygen, very numerous compounds in the organic kingdom. Most of its compounds, except ammonia, are easy of decomposition; none of them are readily formed by direct union of nitrogen, unless in its nascent state.

The *Nitrogen Series of Elements* comprises five perrissads, all acting as triads in their more stable or typical unions, and differing from each other in regular gradation. Some of these progressive variations may be stated as follows:

	N Non-metal.	P Non-metal.	As Non-metal.	Sb Metal.	Bi Metal.
Atomic weights.	14	31	74.9	122	210
Vaporization.	(Gaseous.)	At 288° C.	At 356° C.	At white heat.	At full furnace heat.
Typical hydrides.	$N'''H_3$	$P'''H_3$	$As'''H_3$	$Sb'''H_3$	
	Strong base. Slowly decomposed by electricity.	Weak base. Readily decomposed by electricity.	Indifferent. Decomposed at red heat.	Indifferent. Decomposed below red heat.	
Typical oxygen compounds.	$HN^{V}O_3$	$HP^{V}O_3$	$H_3As^{V}O_4$	Sb'''_2O_3	Bi'''_2O_3
		$H_3P^{V}O_4$	As'''_2O_3		
	Active acid.	Weak acid.	Weak acid.	Indifferent acid.	Not acidulous.
	Soluble salts.	Precipitates.	Precipitates.	Precipitates.	Precipitates.

585. When any dry carbon compound containing nitrogen (organic) is heated with excess of dry sodium hydrate and lime (or any dry, fixed alkali), *ammonia* is evolved, and may be recognized by its odor, effect on moist litmus-paper, etc. (63, 598).

NITRIC ACID.

586. Nitric anhydride, N_2O_5, is a colorless solid, giving off vapor quite freely above 10° C., melting at 30° C., and boiling at 45°, with some decomposition. It is difficult of formation, and does not occur in the changes of ordinary chemical analysis. On contact with water, it forms nitric acid.

587. Absolute nitric acid—$HN^{V}O_3$—is a colorless, transparent, mobile liquid, of the specific gravity of 1.58 at 15° C. [Millon], boiling at 86° C. (187° F.) with partial decomposition, leaving nitric acid mixed with water. Aqueous nitric acid having 70 per cent. of HNO_3, and corresponding to $(HNO_3)_2(H_2O)_3$, specific gravity 1.42, appears to be a definite hydrate; as both stronger and weaker acids are, by boiling, reduced to this composition, which boils at 123° C. (253° F.) The reagent designated in this work as *nitric acid* has a specific gravity of 1.2, and about 35 per cent. of HNO_3—(Fresenius' standard).

588. By heating, by action of the light, and by organic particles from the air, strong nitric acid parts with oxygen and generates nitrous anhydride and nitric peroxide, N_2O_3 and N_2O_4, which remain dissolved with a yellow color. The tendency to this change is very strong in absolute nitric acid, which cannot well be preserved colorless; and the acid of 70 per cent. colors far more readily than that of 35 per cent. The nitrogen oxides may be expelled by boiling; or, with less waste of nitric acid, by passing pure air through it, by means of a bellows, a wash-bottle, and, to avoid dilution, a drying-tube.

589. Nitric acid is *a strong oxidizing agent*, and, as such, its reactions with oxidizable elements and compounds are in constant requisition in analysis. Unless heated, nitric acid does not generally oxidize substances as quickly as chlorine with water.

590. *In oxidizing* and dissolving **metals** or **metalloids**, and in oxidizing **lower oxides**, nitric acid most frequently disengages water and nitric oxide (*d*); but, with certain substances and under certain conditions, other residues are chiefly produced, as dinitrogen tetroxide (*b*), nitrous acid (*c*), nitrous oxide (*e*), nitrogen (*f*), hydrogen (*a*), ammo-

nium nitrate (*g*). Examples of several of these results, as varied by conditions, are seen in the case of zinc (233 *c*, *d*, *e*), iron (168 *b*, *c*, *d*, *e*), tin (426 *d*, *e*), arsenious acid (385 *c*). Further, in the study of oxidations, see 814.

a. $HNO_3 = NO_3$ (combined) $+ H$

b. $2HNO_3 = O$ " $+ H_2O + N_2O_4$

c. $HNO_3 = O$ " $+ HNO_2$ ($2HNO_2 = H_2O$ and N_2O_3)

d. $2HNO_3 = 3O$ " $+ H_2O + 2NO$

e. $2HNO_3 = 4O$ " $+ H_2O + N_2O$

f. $2HNO_3 = 5O$ " $+ H_2O + 2N$ (combined).

g. $10HNO_3 = 8NO_3$ " $+ 3H_2O + NH_4NO_3$

591. The metallic sulphides (except mercuric sulphide) dissolve as nitrates by action of nitric acid, more or less readily; the *sulphur* being at first mostly left as a residue. But as fast as the sulphur is oxidized, metallic *sulphates* are formed, soluble or insoluble (equations in 311).

592. Nitric acid is formed by transposition between sulphuric acid and nitrates:

$KNO_3 + H_2SO_4 = HNO_3 + KHSO_4$
(With solid nitrates, short of a high heat.)

$2KNO_3 + H_2SO_4 = 2HNO_3 + K_2SO_4$
(In solution; or with solids at a red heat.)

593. The **Nitrates** are all soluble in water. There are a few *basic* nitrates —basic bismuth nitrate, basic mercurous and mercuric nitrates, insoluble in water. Many of the nitrates are insoluble in alcohol.

Most of the tests for the **identification** of nitric acid are made by its deoxidation, disengaging a lower oxide of nitrogen (596), or even, by complete deoxidation, forming ammonia (598).

594. Sulphuric acid is transposed with metallic nitrates, with but little decomposition of the nitric acid formed (592). The colorless or slightly reddish gas does not rise till the mixture is very hot—absolute nitric acid not being, like hydrochloric acid, a gas at ordinary temperatures. It reddens litmus, and has a characteristic acrid odor.

595. If, with the sulphuric acid, a bit of **copper** turning, or a crystal of ferrous sulphate, is added to a concentrated solution or residue of nitrate, the mixture gives off abundant brown vapors; the colorless *nitric oxide*, **NO**, which is set free from the mixture, oxidizing immediately in the air to dinitrogen trioxide and tetroxide, N_2O_3 and N_2O_4:

$2KNO_3 + 4H_2SO_4 + 3Cu = K_2SO_4 + 3CuSO_4 + 4H_2O + 2NO$

$2KNO_3 + 4H_2SO_4 + 6FeSO_4 = K_2SO_4 + 3Fe_2(SO_4)_3 + 4H_2O + 2NO$

$2NO + O = N_2O_3$

$2NO + 2O = N_2O_4$

The *three atoms of oxygen, furnished by two molecules of nitrate* (as in 590 *d*), suffice to oxidize three atoms of copper; so that $3CuO$ with $3H_2SO_4$, may form $3CuSO_4$ and $3H_2O$. The same three atoms of oxygen (having six bonds) suffice to oxidize six molecules of ferrous salt into three molecules of ferric salt; so that $6FeSO_4$ with $3H_2SO_4$, can form $3Fe_2(SO_4)_3$ and $3H_2O$.

596. Now if, by the last-named reaction, the nitric oxide is disengaged in cold solution, with excess of ferrous salt and of sulphuric acid, instead of passing off, the nitric oxide combines with the ferrous salt, forming a *black-brown liquid*, $(FeSO_4)_2NO$, decomposed by heat and otherwise instable. And $2NO$ require $4FeSO_4$, in addition to the proportion of ferrous salt in the equation in 595.

$$2KNO_3 + 4H_2SO_4 + 10FeSO_4 = K_2SO_4 + 3Fe_2(SO_4)_3 + 4H_2O + 2(FeSO_4)_2NO$$

This exceedingly delicate test for nitric acid or nitrates in solution may be conducted as follows: Take sulphuric acid to a quarter of an inch in depth in the test-tube; add without shaking a nearly equal bulk of solution of ferrous sulphate, and cool the liquid; then add slowly of the solution to be tested for nitric acid, slightly tapping the test-tube on the side, but not shaking it. The "*brown ring*" forms, between the two layers of liquid—violet, red, brown, or black, according to proportions and conditions. The color disappears on heating, with evolution of nitrous gas, yellowish ferric solution remaining. The test is somewhat more delicate if a crystal of ferrous sulphate be added, instead of the solution, and the test-tube be set aside for several hours.

597. Slight traces of nitrate (as in rain or river-waters) are detected, according to the above reaction, by first reducing to nitrite by heating for some time with **zinc** amalgam, or less readily with finely divided zinc. *Nitrites previously found to be absent*, by the same test, viz.: To a thick layer of the clear filtered water, the solution of ferrous sulphate is added, and the brown coloration obtained, if nitrites have been formed. Or, a drop or two of **potassium iodide** solution with fresh **starch-paste**, and a drop or two of very dilute sulphuric acid is added (607).

The reduction to nitrite may also be effected by **zinc** or **cadmium**, in acidulated solution, as follows (STORER):* Boil the solution, slightly acidulated (by addition of sulphuric acid, if necessary) with metallic cadmium (or zinc) for about five minutes, in a tall vessel —or, better, in a retort with raised condenser, and filter or decant from the metal. Then add a mixture of potassium iodide and starch-paste—or, better, a mixture of zinc iodide, zinc chloride, and starch-paste. The iodine-color indicates nitrous acid, reduced from nitric acid. Without the boiling in acidulate solution, hydrogen peroxide may be formed, giving a fallacious indication for nitric acid.

598. Reduction to Ammonia, by strong reducing agents (590 *g*) is a valuable resource in identifying nitric acid. The tests based on this principle are delicate, but do not distinguish nitric acid from nitrous acid or cyanogen compounds. Ammonia, if found already present, may be distilled off. In those tests requiring use of strong alkali, nitro-

* *Am. Jour. Science*, [3] XII. 176 (Sept., 1876).

genous organic substances will give ammonia. The ammonia obtained is, in most methods, identified by **potassium mercuric iodide**—a reaction so delicate as to show the frequent presence of ammonia in distilled water and many reagents. Hence, all these must be first tested, if necessary, after distillation. Larger quantities of ammonia are recognized in vapor, by litmus, etc.

In neutral solutions, **sodium amalgam** is used as follows—a method for the total of nitric and nitrous acids and ammonia, in potable waters, and otherwise applied: To 6 or 8 cub. cent. (1½ or 2 fluid drachms) of the solution (in a carefully cleaned test-tube), add 100 to 200 grains of sodium-amalgam, which is ½ per cent. sodium: cork the tube lightly and leave for twelve hours. Hydrogen is always slowly evolved, and escapes. Decant and rinse into a glass cylinder one inch wide, and at least six inches high, and add water to about 60 cub. cent. (2 fluid ounces). Nessler's test solution is now applied. The test cannot be made before decantation from the amalgam, as the nascent hydrogen interferes.

The *nascent hydrogen* developed by dissolving **zinc in solution of potassium hydrate** also reduces nitrates in the alkaline solution, and *evolves ammonia.* This is a convenient and efficient test by reduction to ammonia. The solution should be strongly charged with potassium hydrate, the zinc finely divided, and mixed with half its weight of **iron** filings. The mixture is then *distilled* at a boiling rate, and the distillate tested for ammonia by potassium mercuric iodide. The reagents, including the water, should be first tested in the apparatus.

Metallic magnesium may be used for the reduction, as follows: Acidulate with phosphoric acid; add magnesium wire, and leave, cold, a few minutes. Then test for ammonia, by the potassium mercuric iodide solution with potassium hydrate. If interfering acids are present, add potassium hydrate, distil, and test the distillate for ammonia.

Stannous chloride and hydrochloric acid, heated with a nitrate, form stannic chloride, and convert nitric acid to *ammonia* (which remains as ammonium salt).

599. With **hydrochloric acid,** nitric acid forms free chlorine, etc. (nitrohydrochloric acid, 513), applied as a test for nitric acid—in absence of other oxidizing agents—as follows: Heat a little hydrochloric acid in a test-tube to boiling; color it (slightly) with a drop or two of very dilute **indigo solution** (in sulphuric acid), and boil again. If the hydrochloric acid was pure, the color remains unchanged. The addition of a nitrate, with boiling, now quickly bleaches the solution.

600. Phenol, C_6H_5OH, gives a deep red-brown color with nitric acid, by formation of nitrophenol (mono, di, or tri), $C_6H_4(NO_2)OH$ to $C_6H_2(NO_2)_3OH$, "picric acid" or nitrophenic acid. A mixture of one part of phenol (cryst. carbolic acid), four parts of strong sulphuric acid, and two parts of water, constitutes a reagent for a very delicate test for nitrates (or nitrites), a few drops being sufficient. With unmixed nitrates, the action is explosive, unless upon very small quantities. The addition of potassium hydrate deepens and brightens the color of the nitrophenic acid solution.

601. Brucia, dissolved in concentrated sulphuric acid, treated (on a porcelain surface) with even traces of nitrates, gives a fine deep-red color, soon paling to reddish-yellow. If, now stannous chloride dilute solution be added, a fine red-violet color appears. (Chloric acid gives the same reaction.) **Aniline Sulphate** solution, with a half volume of concentrated sulphuric acid, treated (on a porcelain surface) with traces of nitrates, gives a rose-red color, commencing with red lines, and when concentrated appearing brown-red.

602. By slight **ignition,** nitrates of the fixed alkali and alkaline earth metals are reduced to *nitrites,* recognized as shown in **607.** Stronger ignition changes them to *caustic bases,* with formation of brown vapors. Nitrates of heavy metals are mostly changed to *oxides* by heat: ammonium nitrate, wholly to *nitrous oxide* and water.

Heated on Charcoal, or with potassium cyanide, or sugar, sulphur or other easily

oxidizable substance (as in gunpowder), nitrates are reduced with *deflagration or explosion*, more or less violent. With potassium cyanide, on platinum foil, the deflagration is especially vivid. In this reaction, free *nitrogen* is evolved, as by equation *f*, 590.

Strongly heated with excess of potassium hydrate and sugar or other carbonaceous compound, in a dry mixture, nitrates are reduced to *ammonia*, which is evolved, and may be detected. In this carbonaceous mixture, the nitrogen of nitrates reacts with alkalies, like the unoxidized nitrogen in carbonaceous compounds (compare 585, 590 *g*, and 598).

603. **Free Nitric Acid** may be distinguished from nitrates, by giving *the brown liquid* with ferrous salt, on reduction by zinc, *without addition of sulphuric acid*, as stated in 597, and by *coloring quill-cuttings* or white woollen fabrics yellow, when the solution is evaporated with them on the water-bath. The yellow color substance contains xanthoproteic acid, and is formed by action of nitric acid upon any gelatinoid substance —as the skin—and upon ordinary albumenoid substances. (See, also, 678.)

For **Separation** of nitrates from chlorates, see 580.

NITROUS ACID.

604. Absolute nitrous acid, $HN'''O_2$, is hardly known. It may exist in ice-cold, dilute, aqueous solution; but **nitrous anhydride**, N_2O_3, is the more stable compound. The latter, free from water, is a liquid, boiling at −10° C. as gaseous N_2O_3 and N_2O_4, and capable of solution in ice-cold water as a blue liquid. This solution, on slight elevations of temperature, splits into nitric oxide gas and nitric acid, the latter left in solution:

$$3N_2O_3 + H_2O = 2HNO_3 + 4NO$$

605. Likewise, when a metallic nitrite is transposed by dilute sulphuric acid, *nitric oxide* is evolved and *nitric acid* is left in solution; the brown gas which appears being formed by the oxidation of nitric oxide, as soon as it enters the air:

$$6KNO_2 + 3H_2SO_4 = 3K_2SO_4 + 2HNO_3 + 2H_2O + 4NO$$

606. Nitrites, in many relations, act very readily as *oxidizing agents;* in other relations, with equal readiness, as *deoxidizing agents.* In both of these directions, they furnish reactions for their identification. The oxidation changes by nitrous acid are given in 813.

607. By **Oxidizing Action,** nitrites mostly furnish one-fourth of their oxygen, leaving nitric oxide. When decomposed in dilute cold solution by acetic acid or very dilute sulphuric acid, they instantly liberate *iodine* from iodides (*distinction from nitrates,* which give this reaction slowly, even in moderately concentrated solutions). Only a drop or two of the potassium iodide solution should be added; if but traces of nitrite are present, the iodine may be detected by starch or carbon disulphide, as described in 565:

$$HNO_2 + HI = I + H_2O + NO$$

608. Nitrites **with very dilute acids**—and with **acetic acid**—form *the brown liquid* (596) with cold solutions of ferrous salts (distinction from nitrates):

$$6FeSO_4 + 2H_2SO_4 + 2KNO_2 = Fe_2(SO_4)_3 + K_2SO_4 + 2(FeSO_4)_2NO + 2H_2O$$

609. Nitrites, with **iodic acid,** or iodate and slight acidulation, give *free iodine*—a good distinction from nitrates.

610. A concentrated solution of nitrites, treated with a drop or two of **aniline** sul-

phate solution, gives the vapor of phenol, recognized by its odor (C_6H_7N oxidized to C_6H_6O)—a distinction from nitric acid. **Indigo** solution in sulphuric acid is bleached by nitrites.

611. As a reducing agent, a nitrite decolors **potassium permanganate** solution acidulated with sulphuric acid—an easy distinction from nitrate.

612. Nitrites are **all soluble in water**—*argentic nitrite* being but very sparingly soluble, and nitrites generally requiring for solution a larger proportion of water than nitrates. In solutions not very dilute, **silver nitrate** precipitates *silver nitrite*, $AgNO_2$, white. In moderately concentrated solutions of potassium nitrite, **cobalt nitrate** precipitates *potassio cobaltic nitrite*, $(KNO_2)_6Co_2O_3\ (N_2O_3)_2$, reddish-yellow, sparingly soluble in water (225).

In **analysis**, nitrites respond to the common test for nitrates (596); from which they are distinguished as stated in 607 to 611.

613. By ignition, most metallic nitrites are resolved into *metallic oxides, nitrogen*, and *oxygen;* ammonium nitrite, into nitrogen and water. Heated with oxidizable bodies, nitrites deflagrate or detonate, like nitrates.

614. CYANOGEN, $(C''''N''')'$, at ordinary temperatures is a colorless gas, having an odor like prussic acid, and burning in the air with a blue-violet flame—the oxidation of its carbon only. It dissolves freely in water, slowly decomposing in the solution. It is very poisonous. It is not readily decomposed by chlorine in absence of water; but its carbon is oxidized by all strong oxidizing agents, though not rapidly. In many of its combinations, cyanogen resembles chlorine and other halogens.

The most important **Acids of Cyanogen** are :

Hydrocyanic acid $H(CN)'$ or HCy'.

Hydroferrocyanic acid, $H_4Fe''Cy_6$.

Hydroferricyanic acid, $H_6Fe_2^{VI}Cy_{12}$, *or* H_3FeCy_6.

Cyanic acid, $HCyO$.

Sulphocyanic acid, $HCyS$.

HYDROCYANIC ACID.

615. Aosolute hydrocyanic acid, **HCy**, at ordinary temperatures is a colorless liquid, boiling at 27° C. (81° F.), soluble in all proportions in water, alcohol, and in ether—decomposing slightly in its water solutions, scarcely at all in the dark. It vaporizes from its solutions, the more rapidly as they are more concentrated and at higher temperatures, and distils readily unchanged. It has a characteristic odor presented in a modified form by bitter almonds. The pharmacopœial solution, "diluted hydrocyanic acid" (not Scheele's), contains two per cent. of the acid. (The vapor, unless greatly diluted with air, is a quick poison by inhalation: antidotes, chlorine or ammonia, by inhalation.)

616. The **Cyanides** of the alkali metals, alkaline earth metals, and mercuric cyanide, are **soluble in water**—barium cyanide being but sparingly soluble. The solutions are alkaline to test-paper. The other metallic cyanides

are insoluble in water. Many of these dissolve in solutions of alkaline cyanides, by combination, as *double metallic cyanides.*

In **analysis,** the most delicate tests for hydrocyanic acid are the productions of color compounds of iron (622, 621). For the silver precipitate, 619.

617. There are **Two Classes of Double Cyanides,** both of which are formed when a cyanide is precipitated by an alkali cyanide, and redissolved by excess of the precipitant, as shown in equation *a.*

Class I. Double cyanides *which are not affected by alkali hydrates, but suffer dissociation when treated with dilute acids* (*b*). These closely resemble the double iodides (558, potassium mercuric), and the double sulphides or sulphosalts (366 *e*, etc.) The most frequently occurring of the double cyanides of this class, which dissolve in water, are given below.

a. $HgCl_2 + 2KCy = HgCy_2 + 2KCl$

$HgCy_2 + 2KCy = (KCy)_2HgCy_2$

b. $(KCy)_2HgCy_2 + 2HCl = HgCy_2 + 2KCl + 2HCy$

Potassium (or sodium) zinc cyanide, $(KCy)_2ZnCy_2$.

Potassium manganic cyanide (or potassium manganicyanide), $(KCy)_3MnCy_3$.

Potassium (or sodium) nickel cyanide, $(KCy)_2NiCy_2$.

Potassium (or sodium) copper cyanide, $(KCy)_2CuCy_2$.

Potassium cadmium cyanide, $(KCy)_2CdCy_2$.

Potassium (sodium or ammonium) silver cyanide, $KCyAgCy$.

Potassium (or sodium) mercuric cyanide, $(KCy)_2HgCy_2$.

Potassium (or sodium) auric cyanide, $KCyAuCy_3$.

Class II. Double cyanides, *which, as precipitates, are transposed by alkali hydrates, in dilute solution* (*c*), *and are transposed, without dissociation, by dilute acids* (*d*). In these double cyanides, as potassium ferrous cyanide, $(KCy)_4FeCy_2$, the whole of the cyanogen appears to form *a new compound radical* with that metal whose single cyanide is insoluble in water; thus, $FeCy_6$ as "ferrocyanogen," giving K_4FeCy_6 as "potassium ferrocyanide" (for the potassium ferrous cyanide). These more stable double cyanides or "ferrocyanides," etc., correspond to the platinic double chlorides or "chloroplatinates" (480), and the palladium double chlorides, or chloropalladiates (485). The most frequently occurring of the double cyanides of this class, which are soluble in water, are given below.

c. $Cu_2FeCy_6 + 4KOH = 2Cu(OH)_2 + K_4FeCy_6$

d. $K_4FeCy_6 + 2H_2SO_4 = 2K_2SO_4 + H_4FeCy_6$

$2K_3FeCy_6 + 3H_2SO_4 = 3K_2SO_4 + 2H_3FeCy_6$

Alkali ferrocyanides, as $K_4Fe''Cy_6$, potassium ferrous cyanide.

Ferricyanides, as $K_6Fe_2^{VI}Cy_{12}$, or K_3FeCy_6, potassium ferric cyanide.

Cobalticyanides, as $K_6(Co_2)^{VI}Cy_{12}$, or K_3CoCy_6, potassium cobaltic cyanide.

Manganicyanides, as $K_6(Mn_2)^{VI}Cy_{12}$, or K_3MnCy_6, potassium manganic cyanide.

Chromicyanides, as $K_6(Cr_2)^{VI}Cy_{12}$, or K_3CrCy_6, potassium chromic cyanide.

The easily decomposed double cyanides of Class I. are, like the single cyanides, intensely poisonous. The difficultly decomposed double cyanides of Class II. are not poisonous.

618. The **Single Cyanides** are transposed by the **stronger mineral acids,** more or less readily, with liberation of *hydrocyanic acid*, **HCy**, effervescing from concentrated or hot solutions, remaining dissolved in cold and dilute solutions. Mercuric cyanide furnishes **HCy** by action of H_2S, not by other acids. The cyanides of the alkali and alkaline earth metals are transposed by all acids—even the carbonic acid of the air—and exhale the odor of hydrocyanic acid.

619. Solution of silver nitrate precipitates, from solutions of cyanides or of hydrocyanic acid (not from mercuric cyanide), *silver cyanide*, **AgCy**, white, insoluble in dilute nitric acid, soluble in ammonium hydrate, in hot ammonium carbonate, in potassium cyanide, and in thiosulphates—uniform with silver chloride. Cold strong hydrochloric acid decomposes it with evolution and odor of hydrocyanic acid (recognition *from chloride*); and when well washed, and then gently ignited, it does not melt, but leaves metallic silver, soluble in dilute nitric acid, and precipitable as chloride (distinction and means of separation from chloride).

620. Solution of **mercurous nitrate,** with cyanides or hydrocyanic acid, is resolved into *metallic mercury*, as a gray precipitate, and mercuric cyanide and nitrate, in solution. Salts of **copper** react, as stated in 278; salts of **lead,** as stated in 318.

621. Ferrous salts, added to saturation, precipitate from solutions of cyanides, not from hydrocyanic acid, *ferrous cyanide*, $FeCy_2$, white, if free from the ferric hydrate formed by admixture of ferric salt, and, with the same condition, soluble in excess of the cyanide, as (with potassium cyanide), $(KCy)_4$-$FeCy_2 = K_4FeCy_6$, potassium *ferrocyanide* (*a*). On acidulating this solution, it gives the blue precipitates with iron salts, more marked with ferric salts (*b*):

a. $2KCy + FeSO_4 = FeCy_2 + K_2SO_4$

$FeCy_2 + 4KCy = K_4FeCy_6$

b. $3K_4FeCy_6 + 2Fe_2Cl_6 = Fe_4(FeCy_6)_3 + 12KCl$

This *production of the blue ferric ferrocyanide is made a delicate test for hydrocyanic acid,* as follows: A little potassium hydrate and ferrous sulphate are added, the mixture digested warm for a short time; then a very little ferric chloride is added, and the whole slightly acidulated (so as to dissolve all

the ferrous and ferric hydrates), when prussian blue will appear, if hydrocyanic acid was present.

622. *The production of the red ferric sulphocyanate is a test for hydrocyanic acid, more delicate* than formation of ferrocyanide. By warm digestion this reaction occurs: $KCy + S = KCyS$; or:

$$(NH_4)_2S_4 + 2HCy = 2NH_4CyS + H_2S + S$$

To the material in an evaporating dish, add one or two drops of **yellow ammonium sulphide**, and digest on the water-bath until the mixture is colorless, and free from sulphide. Slightly acidulate with hydrochloric acid (which should not liberate H_2S), and add a drop of solution of ferric chloride; the blood-red solution of ferric sulphocyanate will appear, if hydrocyanic acid was present.

623. Solution of **nitrophenic acid**, $C_6H_2(NO_2)_3OH$, added, in a small quantity, to a neutralized solution of cyanides of alkali metals, on boiling (and standing), gives a blood-red color, due to picrocyanate (as $KC_8H_4N_5O_6$). This test is very delicate, but not very distinctive, as various reducing agents give red products with nitrophenic acid.

624. The **fixed alkali hydrates**, in boiling solution, strongly alkaline, gradually decompose the cyanides with production of *ammonia* and formate. Ferrocyanides and ferricyanides finally yield the same products. Dilute alkalies, not heated, transpose, as by equation *c*, 617.

$$HCN + KOH + H_2O = KCHO_2 + NH_3$$

By fusion with alkali hydrates, all cyanogen compounds yield ammonia (585). **Concentrated sulphuric acid** decomposes cyanogen in all of its compounds.

625. Cyanides are **Reducing Agents**—in the wet way having a moderate, in the dry way a forcible action; and in either way removing sulphur, as well as oxygen (830):

With oxides: $O + KCy = KCyO$

With sulphides: $S + KCy = KCyS$

In solution: cyanides decolorize the **permanganate**, but do not reduce the cupric hydrate with potassium hydrate.

By fusion: cyanides are employed as the most efficient of agents for obtaining metals from their oxides or sulphides, as has been stated with reference to arsenic, tin, etc. The cyanates and sulphocyanates, so formed, are not readily decomposed by heat alone.

By exposure to the air, cyanides acquire some proportion of cyanates, and commercial cyanide of potassium contains cyanate.

HYDROFERROCYANIC ACID.

626. Absolute hydroferrocyanic acid, H_4FeCy_6—see 617, Class II.—is a white solid, freely soluble in water and in alcohol. The solution is strongly acid to test-paper, and decomposes carbonates with effervescence, and acetates. It is non-volatile, but absorbs oxygen from the air, more rapidly when heated, evolving hydrocyanic acid and depositing prussian blue, thus:

$$7H_4FeCy_6 + 2O = Fe_4(FeCy_6)_3 + 2H_2O + 24HCy$$

627. Hydroferrocyanic acid is formed by transposition of metallic ferrocyanides in solution, with strong acids (*a*). When the solution is heated, hydrocyanic acid is evolved; in the case of an alkali ferrocyanide, without absorption of oxygen (*b*). Potassium ferrocyanide and sulphuric acid are usually employed for preparation of hydrocyanic acid :

a. $K_4FeCy_6 + 2H_2SO_4 = 2K_2SO_4 + H_4FeCy_6$

b. $3H_4FeCy_6 + K_4(FeCy_6) = 2K_2FeFeCy_6 + 12HCy$

a. and *b.* $2K_4FeCy_6 + 3H_2SO_4 = 3K_2SO_4 + K_2FeFeCy_6 + 6HCy$

628. The **Ferrocyanides** of the alkali metals, strontium, calcium, and magnesium, are freely **soluble in water**; of barium, sparingly soluble; of the other metals, insoluble in water. There are *double ferrocyanides;* soluble and insoluble; that of barium and potassium is soluble, but *potassio calcic ferrocyanide* is insoluble. The most of the ferrocyanides of a heavy metal and an alkali metal are insoluble. Potassium and sodium ferrocyanides are precipitated from their water solutions by alcohol (distinction from ferricyanides).

The soluble ferrocyanides are yellowish in solution and in crystals, white when anhydrous. The *insoluble ferrocyanides* have marked and very diverse **colors**—as seen below.

In **analysis**, soluble ferrocyanides are recognized by their reactions with ferrous and ferric salts and copper salts (629). Separated from ferricyanide, by insolubility of alkali salt in alcohol.

629. Solutions of alkali **Ferrocyanides**, as K_4FeCy_6, give, with soluble salts of:

Aluminium,	a white precipitate,	$Al_2(OH)_6$ and $FeCy_2$ (formed slowly).
Antimony,	a white "	
Bismuth,	a white "	$Bi_4(FeCy_6)_3$.
Cadmium,	a white "	Cd_2FeCy_6 (sol. in hydrochloric acid).
Calcium,	a white "	$K_2CaFeCy_6$.
Chromium,	no "	
Cobalt,	a green, then gray "	Co_2FeCy_6.
Copper,	a red-brown "	Cu_2FeCy_6.
Gold,	no "	
Iron (ferrous),	whi. then blue "	$K_2FeFeCy_6$.
Iron (ferric),	a deep blue "	$Fe_4(FeCy_6)_3$.
Lead,	a white "	Pb_2FeCy_6.
Magnesium,	a white "	$(NH_4)_2MgFeCy_6$ (in presence of NH_4).
	a yellow-white "	$K_2MgFeCy_6$ (only in conc. solution).

Manganese, a white precipitate	Mn_2FeCy_6 (sol. in hydrochloric acid).
Mercury (mercurous), a whi. "	Hg_4FeCy_6 (gelatinous).
Mercury (mercuric), a white "	Hg_2FeCy_6, turning to $HgCy_2$ and $Fe_3(FeCy_6)_2$, blue.
Molybdenum, a brown "	
Nickel, a greenish-white "	Ni_2FeCy_6.
Silver, a white "	Ag_4FeCy_6 (slowly turning blue).
Tin (stannous, stannic), whi. "	(gelatinous).
Uranium (uranous), brown "	$UFeCy_6$.
Uranium (uranic), red-brown "	$U_2(FeCy_6)_3$.
Zinc, a white, gelatinous "	Zn_2FeCy_6.

Insoluble ferrocyanides are transposed by **alkalies** (617 *c*, and 624).

630. It will be observed (617) that *ferrocyanides are ferrous* combinations, while *ferricyanides are ferric* combinations. And, although ferrocyanides are far less easily oxidized than simple ferrous salts, being stable in the air, they are nevertheless **reducing agents**—of moderate power. For oxidations of ferrocyanides, see 832.

$$K_4(FeCy_6)'''' + Cl = K_3(FeCy_6)''' + KCl$$

HYDROFERRICYANIC ACID.

631. Absolute hydroferricyanic acid, H_3FeCy_6, is a non-volatile, crystallizable solid, readily soluble in water, with a brownish color, and an acid reaction to test-paper. It is decomposed by a slight elevation of temperature. In the transposition of most ferricyanides, by sulphuric or other acid, the hydroferricyanic acid radical is broken up.

632. The **Ferricyanides** of the metals of the alkalies and alkaline earths are **soluble in water**; those of most of the other metals are insoluble or sparingly soluble. Potassium and sodium ferricyanides are but slightly, or not at all, precipitated from their water solutions by **alcohol** (separation from ferrocyanides).

In **analysis**, the reactions with ferrous and ferric salts are distinguishing.

The soluble ferricyanides have a red color, both in crystals and solution; those insoluble have different, strongly marked colors.

Ferricyanides are not easily decomposed by dilute acids; but alkali hydrates either transpose them (617 *c*), or decompose their radicals (624)

Solutions of metallic **Ferricyanides** give, with soluble salts of:

Aluminium, no precipitate.

Antimony, no precipitate.

Bismuth, light-brown precipitate, $BiFeCy_6$—insol. in hydrochloric acid.

Cadmium, yellow precipitate, $Cd_3(FeCy_6)_2$—sol. in acids and in ammonia.

Chromium, no precipitate.

Cobalt, brown-red precipitate, $Co_3(FeCy_6)_2$—insoluble in acids. With ammonium chloride and hydrate, excess of ferricyanide gives a blood-red solution, a distinction of cobalt, from nickel, manganese and zinc.

Copper, yellow-green precipitate, $Cu_3(FeCy_6)_2$—insol. in hydrochl. acid.

Gold, no precipitate.

Iron (ferrous), dark-blue precipitate, $Fe_3(FeCy_6)_2$—insoluble in acids.

Iron (ferric), no precipitate, a darkening of the liquid.

Lead, no precipitate, except in concentrated solutions (dark brown).

Manganese, brown precipitate, $Mn_3(FeCy_6)_2$—insoluble in acids.

Mercury (mercurous), red-brown precipitate, turning white on standing.

Mercury (mercuric), no precipitate.

Nickel, yellow-green precipitate, $Ni_3(FeCy_6)_2$—insol. in hydrochloric acid. With ammonium chloride and hydrate, excess of ferricyanide gives a copper-red precipitate.

Silver, a red-brown precipitate, Ag_3FeCy_6—soluble in ammonia.

Tin (stannous), white precipitate, $Sn_3(FeCy_6)_2$—sol. in hydrochloric acid.

Tin (stannic), no precipitate.

Uranium (uranous), no precipitate.

Zinc, orange precipitate, $Zn_3(FeCy_6)_2$—soluble in hydrochloric acid and in ammonia.

633. Ferricyanides, as *ferric* combinations, are capable of acting as **Oxidizing Agents**, the radical $(FeCy_6)'''$, becoming $(FeCy_6)''''$, and taking another portion of metal into combination, forming ferrocyanides (compare 630). Products with reducing agents are given in 833.

$$4K_3FeCy_6 + 2H_2S = 3K_4FeCy_6 + H_4FeCy_6 + 2S$$

$$K_3FeCy_6 + KI = K_4FeCy_6 + I$$

Nitric acid, or acidulated nitrite, by continued digestion in hot solution, effects a still higher **Oxidation of Ferricyanides**, with the production, among other products, of *nitro-ferricyanides* or *nitro-prussides*. These salts are generally held to have the composition represented by the acid, $H_2Fe''(NO)'Cy_5$. *Sodium Nitroprusside* is used as a reagent for soluble sulphides—that is, in presence of alkali hydrates, a test for hydrosulphuric acid; in presence of hydrosulphuric acid, a test for alkali hydrates (668).

CYANIC ACID.

634. Absolute cyanic acid, **HCyO**, is a colorless liquid, giving off pungent, irritating vapor, and only preserved at very low temperatures. It cannot be formed by transposing metallic cyanates with the stronger acids in the presence of water, by which it is changed into carbonic anhydride and ammonia :

$$H(CN)O + H_2O = NH_3 + CO_2.$$

635. The **Cyanates**, therefore, when treated with hydrochloric or sulphuric acid, effervesce with the escape of *carbonic anhydride* (distinction from cyanides), the pungent *odor of cyanic acid* being perceptible. The *ammonia* remains in the liquid as ammonium salt, and may be detected by addition of potassium hydrate, with heat.

$$2K(CN)O + 2H_2SO_4 + 2H_2O = K_2SO_4 + (NH_4)_2SO_4 + 2CO_2$$

636. The cyanates of the metals of the alkalies and of calcium are soluble in water; most of the others are insoluble or sparingly soluble. All the solutions gradually decompose, with evolution of ammonia.—*Silver cyanate* is sparingly soluble in hot water, readily soluble in ammonia; soluble, with decomposition, in dilute nitric acid (distinction from cyanide). *Copper cyanate* is precipitated greenish-yellow.

Ammonium cyanate in solution changes gradually, or immediately when boiled, to *urea*, or carbamide, with which it is isomeric : $NH_4CNO = (NH_2)'_2(CO)''$. The latter is recognized by the characteristic crystalline laminæ of its nitrate, when a few drops of the solution, on glass, are treated with a drop of nitric acid. Also, solution of urea with solution of mercuric nitrate, forms a white precipitate, $CH_4N_2O(HgO)_2$, not turned yellow (decomposed) by solution of sodium carbonate (no excess of mercuric nitrate being taken). Solution of urea, on boiling, is resolved into ammonium carbonate, which slowly vaporizes :

$$CH_4N_2O + 2H_2O = (NH_4)_2CO_3$$

637. Cyanates, in the dry way, are reduced by strong deoxidizing agents to cyanides.

SULPHOCYANIC ACID (THIOCYANIC ACID).

638. This acid, **HCyS**, corresponds to cyanic acid (**HCyO**), oxygen being substituted by sulphur. Its salts, the sulphocyanates (also termed *sulphocyanides*), appear to be constituted as sulphosalts, with **CyS** as the acid radical. In this view, they are not haloid salts.

639. Absolute sulphocyanic acid, **HCyS**, is a colorless liquid, crystallizing at 12° C. (54° F.), and boiling at 85° C. (185° F.) It has a pungent, acetous odor, and reddens litmus. It is soluble in water. The absolute acid decomposes quite rapidly at ordinary temperatures; the dilute solution, slowly; with evolution of carbonic anhydride, carbon disulphide, hydrosulphuric acid, hydrocyanic acid, ammonia, and other products.

640. The same products result, in greater or less degree, from transposing *soluble* **Sulphocyanates** with strong acids; in greater degree as the acid is stronger and heat applied; while in dilute cold solution, the most of the sulphocyanic acid remains undecomposed, giving the acetous odor (see 643). The sulphocyanates *insoluble* in water, are not all readily transposed by acids. Sulphocyanates of metals, whose sulphides are insoluble in certain acids, resist the action of the same acids.

641. The sulphocyanates of the metals of the alkalies, alkaline earths; also, those of iron (ferrous and ferric), manganese, zinc, cobalt, and copper—are **soluble in water.** Mercuric sulphocyanate, sparingly soluble; potassio mercuric sulphocyanate, more soluble. *Silver sulphocyanate* is insoluble in water, insoluble in dilute nitric acid, slowly soluble in ammonium hydrate. The ferric reaction is the most **distinctive.**

642. Solutions of metallic **Sulphocyanates** give, with soluble salts of:

Cobalt, very concentrated, a blue color, $Co(CyS)_2$, crystallizable in blue needles, soluble in alcohol, not in carbon disulphide. The coloration is promoted by warming, and the test is best made in an evaporating dish. In strictly neutral solutions, iron, nickel, zinc, and manganese, do not interfere (Schoenn).

Copper, if concentrated, a black crystalline precipitate, $Cu(CyS)_2$, soluble in sulphocyanate. With **sulphurous acid,** a white precipitate, **CuCyS.**

Iron (ferrous), no precipitate or color.

Iron (ferric), an intensely blood-red solution of $Fe_2(CyS)_6$, decolored by solution of **mercuric chloride** (189, *distinction from acetic acid*); decolored by phosphoric, arsenic, oxalic, and iodic acids, etc., unless with excess of ferric salt; decolored by alkalies, and by nitric acid, not by dilute hydrochloric acid. On introduction of metallic zinc, it evolves hydrosulphuric acid. Ferric sulphocyanate is soluble in **ether,** which extracts traces of it from aqueous mixtures, rendering its color much more evident by the concentration in the ether layer.

Lead, gradually, a yellowish crystalline precipitate, $Pb(CyS)_2$, changed by boiling to white basic salt.

Mercury (mercurous), a white precipitate, **HgCyS,** resolved by boiling into Hg and $Hg(CyS)_2$. The mercurous sulphocyanate, **HgCyS,** swells greatly *on ignition* (being used in "Pharaoh's serpents"), with evolution of mercury, nitrogen, sulphocyanogen, cyanogen, and sulphur dioxide.

Mercury (mercuric), in solutions not very dilute, a white precipitate $Hg(CyS)_2$, somewhat soluble in excess of the sulphocyanate, sparingly soluble in water, moderately soluble in alcohol. On ignition, it swells like the mercurous precipitate.

Platinum. Platinic chloride, gradually added to a hot, concentrated solution of potassic sulphocyanate, forms a deep-red solution of double sulphocyanate of potassium and platinum $(KCyS)_2Pt(CyS)_4$, or more properly, $K_2Pt(CyS)_6$, the *sulphocyano-platinate of*

potassium. The latter salt gives bright-colored precipitates with metallic salts. The sulphocyano-platinate of lead (so formed) is golden-colored; that of silver, orange-red.

Silver, a white precipitate, **AgCyS**, insoluble in water, insoluble in dilute nitric acid, slowly soluble in ammonium hydrate, readily soluble in excess of potassic sulphocyanate; blackens in the light.

643. Certain active oxidizing agents, viz.: nascent chlorine, and nitric acid containing nitrogen oxides, acting in hot, concentrated solution of sulphocyanates, precipitate *persulphocyanogen*, $H(CyS)_3$, of a yellow-red to rose-red color, even blue sometimes, when concentrated. It may be formed in the test for iodine, and mistaken for that element, in starch or carbon disulphide. If boiled with solution of potassium hydrate, it forms sulphocyanate.

Concentrated hydrochloric acid, or sulphuric acid, added in excess to water solution of sulphocyanates, causes the gradual formation of a yellow precipitate, *persulphocyanic acid*, $(HCy)_2S_3$, slightly soluble in hot water, from which it crystallizes in yellow needles. It dissolves in alcohol and in ether.

644. Sulphocyanate of potassium can be fused in close vessels, without decomposition; but with free access of air, it is resolved into sulphate and cyanate, with evolution of sulphurous acid.

645. CARBON is a solid, characterized by being insoluble in acids, alkalies, or other ordinary solvents, and infusible and non-volatile at very high temperatures. It suffers no oxidation in the air at ordinary temperatures.—As *charcoal*, the black residue of the partial combustion of all organic substances, carbon is quickly oxidized to *carbonic anhydride* in the air at the temperature of ignition, but is not affected by powerful oxidizing solvents.—As *graphite*, carbon is only very slowly oxidized during ignition in the air, but is gradually oxidized by repeated digestions with chlorates and strong acids.

The **Acids containing Carbon,** whose reactions are given in this work are:

Carbonic acid, $H_2C''''O_3$; anhydride, $C''''O_2$.

Oxalic acid, $H_2C_2^{VI}O_4$.*

The Cyanogen acids, named in 614.

Acetic acid, $H(C_2H_3O_2)'$.

Tartaric acid, $H_2(C_4H_4O_6)''$.

Citric acid, $H_3(C_6H_5O_7)'''$.

* In the received view, that carbon remains a tetrad in nearly all its many compounds, the following graphic formulæ are written:

Carbonic acid, $\begin{matrix} H-O- \\ \\ H-O- \end{matrix}\!\!>C=O$

Oxalic acid, $\begin{matrix} H-O-C=O \\ \quad\quad\quad | \\ H-O-C=O \end{matrix}$

Compare with pseudo-triads, page 11, foot-note.

CARBONIC ANHYDRIDE.

646. Absolute carbonic acid, as H_2CO_3, is not known.—**Carbonic anhydride**, CO_2, carbon dioxide, or "anhydrous carbonic acid," is **a gas** at atmospheric temperatures and pressures, and dissolving, however much condensed, in about its own bulk of water. The alkali metals form double carbonates with hydrogen, or acid carbonates, as $KHCO_3$. The anhydride, CO_2, is often designated as carbonic acid, as we have no other substance to which the term can be applied.

647. The **Carbonates** of the metals of the alkalies are very freely **soluble in water**; the hydrogen carbonates of the same metals, moderately soluble in water. *All other metallic carbonates are insoluble in water.* The carbonates of the alkaline earth metals, and of some others, dissolve slightly in water saturated with carbonic acid, and to a greater extent in water saturated with compressed carbonic acid—from which solutions they are fully precipitated on heating in open vessels. The metallic carbonates, except normal ammonium carbonate, are insoluble in *alcohol.*

In **analysis**, the carbonates are denoted by the sudden effervescence, etc. (648), caused even by acetic acid.

648. The carbonates, both soluble and insoluble, are decomposed by **all the acids** (except hydrosulphuric and hydrocyanic), even when very dilute. The decomposition is attended by *sudden effervescence of carbonic anhydride*, CO_2, which reddens moist **litmus** (*a*).

With normal carbonates in cold solution, slight additions of acid (short of a saturation of half the base) do not cause effervescence, because acid carbonate is formed (*b*); and when there is much free alkali present (as in testing caustic alkalies for slight admixtures of carbonate), perhaps no effervescence is obtained. By the time all the alkali is saturated with acid, there is enough water present to dissolve the little quantity of gas set free. But if the carbonate *solution is added drop by drop to the acid*, so that the latter is constantly in excess, even slight traces of carbonate give notable effervescence.

a. $K_2CO_3 + 2HCl = 2KCl + H_2O + CO_2$

b. $K_2CO_3 + HCl = KCl + KHCO_3$

649. *The effervescence of carbonic acid gas*, CO_2, is distinguished from that of H_2S or SO_2 by the gas being *odorless*, from that of N_2O_3 by its being *colorless* and odorless; from all others by the effervescence being proportionally more *forcible.* It should be remembered, however, that CO_2 is evolved (with CO) on adding strong sulphuric acid to *oxalates* (653), or to cyanates (635).

On passing the gas, CO_2, into **solution of calcium hydrate** (*a*); or of **barium hydrate** (*b*); or into solutions of calcium or barium chloride, containing much ammonium hydrate (*c*), or into **ammoniacal solution of lead**

acetate (*d*); a white precipitate or turbidity of *insoluble carbonate* is obtained. In the case of the solution of lime (or of baryta if dilute), the precipitate is soluble in sufficient excess of the gas—*i.e.*, in water saturated with carbonic acid; but it is not easy to saturate with gas generated in an open test-tube. The precipitate may be obtained by *decanting* the gas (one-half heavier than air) from the test-tube in which it is liberated into a (wide) test-tube, containing the solution to be precipitated; but the operation requires a little perseverance, with repeated generation of the gas, owing to the difficulty of displacing the air by pouring into so narrow a vessel. The result is controlled better, by generating the gas in a large test-tube, having a stopper bearing a narrow delivery-tube, so bent as to be turned down into the solution to be precipitated:

a. $CO_2 + Ca(OH)_2 = CaCO_3 + H_2O$

b. $Ba(OH)_2$ giving $BaCO_3$

c. $CO_2 + CaCl_2 + 2NH_4OH = CaCO_3 + 2NH_4Cl + H_2O$

d. $CO_2 + Pb_2O(C_2H_3O_2)_2 = PbCO_3 + Pb(C_2H_3O_2)_2$

The solutions of calcium and barium hydrates, furnish more *delicate tests for carbonic anhydride* than the ammoniacal solutions of calcium and barium chlorides, but less delicate than lead basic acetate solution. The latter is so rapidly precipitated by atmospheric carbonic anhydride, that it cannot be preserved in bottles partly full and frequently opened, and cannot be diluted clear, unless with recently boiled water.

650. *Solutions of the acid carbonates effervesce*, with escape of CO_2, on boiling or heating, thus:

$2KHCO_3 = K_2CO_3 + H_2O + CO_2$. (Gradually, at 100° C.)

$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$. (Gradually, at 70° C.; rapidly at 90° to 100° C.)

$2NH_4HCO_3 = (NH_4)_2CO_3 + H_2O + CO_2$. (Begins to evolve CO_2 at 36° C.)

$(NH_4)_4H_2(CO_3)_3 = 2(NH_4)_2CO_3 + H_2O + CO_2$. (Begins at 49° C.)

651. *Solutions of carbonates form precipitates with* salts of all metals, except those of the alkalies; the precipitate being, in the larger number of cases, *a carbonate or basic carbonate;* in some cases, *a hydrate*, with effervescence of CO_2:

$K_2CO_3 + FeCl_2 = FeCO_3 + 2KCl$

$3K_2CO_3 + Fe_2Cl_6 + 3H_2O = Fe_2(OH)_6 + 6KCl + 3CO_2$

652. On ignition, the normal carbonates of the metals of the fixed alkalies are not decomposed; the carbonates of barium, strontium, and calcium are dissociated slowly, at white heat (81); all other carbonates are readily broken up.

OXALIC ACID.

653. Absolute oxalic acid, $H_2C_2O_4$, is a white, amorphous solid, which by care may be sublimed with only partial decomposition (*a*), at about 165° C. (329° F.) *Crystallized oxalic acid*, $H_2C_2O_4.2H_2O$, effloresces very slowly in warm dry air, and melts in its crystallization-water at 98° C. (208° F.); at which temperature the liquid soon evaporates to the absolute acid. Oxalic anhydride is not formed.

$$a. \quad H_2C_2O_4 = H_2O + CO_2 + CO$$

Concentrated sulphuric acid, with a gentle heat, decomposes *oxalic acid,* with effervescence of *carbon dioxide and carbon monoxide,* according to the equation in the preceding paragraph. With *oxalates,* the decomposition generates the same gases. Other strong dehydrating agents produce the same result.

The *effervescing gas,* $CO_2 + CO$, gives the reactions for carbonic anhydride (649); also, if in a sufficient quantity, it will *burn with a blue flame,* when ignited, by the oxidation of the carbon monoxide.

654. The **Oxalates** of the metals of the alkalies are **soluble in water;** nearly all those of the other metals are either insoluble or sparingly soluble in water. (Chromic oxalate is freely soluble in water; magnesic oxalate, sparingly soluble.)

In **analysis,** calcium oxalate is the precipitate most used, soluble in hydrochloric, not in acetic, acid. Also, the reducing action (657), decomposition with sulphuric acid (653), and ignition (658), serve in identification.

655. The metallic oxalates, soluble and insoluble, are transposed by **dilute sulphuric, hydrochloric,** and **nitric** acids, with formation of *oxalic acid:*

$$CaC_2O_4 + 2HCl = CaCl_2 + H_2C_2O_4$$

That is: the precipitated oxalates of those metals, which form soluble chlorides, *dissolve in dilute hydrochloric acid;* of those metals which form soluble sulphates, in dilute sulphuric acid; and all precipitated oxalates dissolve in dilute nitric acid.

Acetic acid does not dissolve precipitated oxalates, or but slightly. Certain of the oxalates dissolve, to some extent, in **oxalic acid** (as acid oxalates).

656. The *precipitates of oxalates are white.* It follows, from 655, that solution of *oxalic acid* can be precipitated but very slightly by any metallic salts of the stronger acids.

Solutions of metallic *oxalates* give, with soluble **salts of calcium,** a quite complete precipitate of *calcium oxalate,* CaC_2O_4 (compare 107); with **salts of barium,** in solutions not very dilute, a slightly soluble precipitate of *barium oxalate,* BaC_2O_4; with **ferric salts,** a yellowish-white precipitate of *ferric oxa-*

late, $Fe_2(C_2O_4)_3$, sparingly soluble in water, soluble in free oxalic acid; **with ferrous salts**, a yellowish precipitate of *ferrous oxalate*, FeC_2O_4, not soluble in oxalic acid; with salts of **lead**, as stated in 317; with salts of **silver**, a characteristic reaction, as stated in 337 and 658 *c*.

657. Oxalic acid is a decided **Reducing Agent**, being converted to *water and carbonic anhydride* (*a*), and the metallic oxalates to *carbonates and carbonic anhydride* (*b*), by all strong oxidizing agents. The action of oxidizing agents is given in 811.

a. $H_2C_2O_4 + O = H_2O + 2CO_2$

b. $K_2C_2O_4 + O = K_2CO_3 + CO_2$

658. The oxalates are all dissociated on ignition. Those of the metals of the alkalies and alkaline earths are resolved at an incipient red heat, into carbonates and carbon monoxide (*a*)—a higher temperature decomposing the carbonates (652). The oxalates of metals, whose carbonates are easily decomposed, but whose oxides are stable, are resolved into oxides, carbonic anhydride, and carbon monoxide (*b*). The oxalates of metals, whose oxides are decomposed by heat, leave the metal, and give off carbonic anhydride (*c*). As an example of the latter class, *silver oxalate*, when heated before the blow-pipe, decomposes explosively, with a sudden puffing sound—a test for oxalates:

a $CaC_2O_4 = CaCO_3 + CO$

b. $ZnC_2O_4 = ZnO + CO_2 + CO$

c. $Ag_2C_2O_4 = 2Ag + 2CO_2$

659. SULPHUR is a solid—in yellow, brittle, friable *masses* (from melting); or in yellowish, gritty *powder* (from sublimation); or in nearly white, slightly cohering, finely crystalline *powder* (by precipitation from its compounds). It melts at about 111° C. (232° F.); at higher temperatures, it suffers peculiar physical modifications of consistence, etc.; and distils at 445° C. (836° F.) It is not sensibly volatile at ordinary temperatures, but has a slight, characteristic odor.

In chemical activity, volatility, and other properties, sulphur stands as the second member of the Oxygen Series: O, 16; S, 32; Se, 78; Te, 128.

660. Sulphur is insoluble in water; slightly soluble in alcohol and in ether, freely soluble in carbon disulphide; but with physical solvents other than water, its different modifications have different solubilities.

661. *By combination*—sulphur *dissolves* readily in hot solutions of hydrates of potassium, sodium, calcium, or barium, forming *supersulphides and thiosulphates* (*a*). These can be separated by alcohol, in which the sulphides dissolve. Sulphur is acted upon slowly by active oxidizing agents, as hot concentrated nitric acid (*b*), or chlorine generated in presence of water (*c*), with formation of *sulphuric acid*. Hot concentrated sulphuric acid very slowly oxidizes sulphur to *sulphurous anhydride*, by its own reduction to the same compound (*d*):

a. $3Ca(OH)_2 + 6S = 2CaS_2 + CaS_2O_3 + 3H_2O$

Or: $3Ca(OH)_2 + 12S = 2CaS_5 + CaS_2O_3 + 3H_2O$

b. $S + 2HNO_3 = H_2SO_4 + 2NO$

c. $S + 6Cl + 4H_2O = H_2SO_4 + 6HCl$

d. $S + 2H_2SO_4 + H_2O = 3H_2SO_3$

662. In the air, at ordinary temperatures, finely divided sulphur is very slightly oxidized, by ozone, to *sulphuric acid;* at about 260° C. (500° F.) it begins to oxidize rapidly to *sulphurous anhydride,* burning with a blue flame.

The principal **Acids of Sulphur** are:

Hydrosulphuric acid, H_2S''.

Sulphuric acid, $H_2S^{VI}O_4$.

Sulphurous acid, $H_2S''''O_3$.

Thiosulphuric acid, $H_2S_2''''O_3$.

Dithionic acid, $H_2S_2O_6$.

Trithionic acid, $H_2S_3O_6$.

Tetrathionic acid, $H_2S_4O_6$.

Pentathionic acid, $H_2S_5O_6$.

HYDROSULPHURIC ACID.

663. Absolute hydrosulphuric acid, H_2S, is a colorless gas, sparingly soluble in water.*

The solution in open vessels **vaporizes** gas constantly, at ordinary temperatures, until exhausted; more rapidly when boiled. Both gas and solution feebly redden moist **litmus-paper**; and have a very strong, characteristic odor. (The concentrated gas is a quick poison, by inhalation.)

Absolute hydrosulphuric acid is combustible in the air—burning with a blue flame, to sulphurous anhydride and water.

664. The **solubility** of the **Metallic Sulphides** in water, dilute acids, hot nitric acid, and in alkali sulphides, is shown in the grouping of the bases, and the sub-grouping of the second group precipitates.

In **analysis,** sulphides are known by generation of H_2S (665), or separation of **S** by oxidizing solvents, and by the color test with nitro-ferricyanide (668).

665. Sulphuric acid, dilute, transposes the metallic sulphides; except those of arsenic, tin, antimony, mercury, silver, (and lead), which are decomposed with difficulty, or not at all:

$$FeS + H_2SO_4 = FeSO_4 + H_2S$$

The gaseous hydrosulphuric acid, when liberated, is recognized by its *odor,*

* One part of iron sulphide, with one and a half parts of concentrated sulphuric acid diluted to eight or nine parts, generate sufficient hydrosulphuric acid to saturate fifty parts of water at medium temperature.

by blackening paper moistened with **lead acetate**, or with a solution of a **lead salt with excess of hydrate of potassium** or sodium (311 and 309). In the detection of traces of the gas, a slip of bibulous paper, so moistened, may be inserted into a slit in the smaller end of a cork, which is fitted to the test-tube, wherein the material to be tested is treated with sulphuric acid; the tube being set aside in a warm place for several hours. A very delicate test is made by conducting the gas into ammoniacal solution of nitroferricyanide (668).

If any oxidizing agents are present—as chromates, ferric salts, manganic salts, chlorates, etc.—hydrosulphuric acid is not generated, but instead sulphur is separated, or sulphates are formed (666).

The sulphides not transposed with hydrochloric or sulphuric acid, are recognized by the *separation of sulphur* on treatment with **nitric acid**, or with **nitrohydrochloric acid**. Also, these sulphides and certain supersulphides, attacked with difficulty by acids, as *iron pyrites* and *copper pyrites*, are reduced and dissolved, with evolution of *hydrosulphuric acid*, by **dilute sulphuric acid with zinc**. The gas, with its excess of hydrogen, may be tested by 668.

666. Hydrosulphuric acid is a strong **reducing agent**, and the metallic sulphides act in the same capacity with a greater or less degree of force. The reactions with oxidizing agents are given at length in 817. Equations are given —with **ferric salts**, in 171 *a*; with **chromates**, in 166 *a*; with **iodic acid**, in 571 *c*, *d*; with **iodine**, in 554 *e*; with **sulphurous acid**, in 694 *c*; with **ferricyanides**, in 633. Iodine solutions and **permanganate** solutions are quickly *decolored* with precipitation of sulphur.

The hydrogen of H_2S takes oxygen readily; the sulphur more slowly. In the oxidation of metallic *sulphides*, generally, less sulphur is left unoxidized than occurs in the oxidation of hydrosulphuric acid—owing to the stronger tendency to form *sulphates*.

667. Solutions of metallic sulphides give precipitates with soluble **salts of second and third group metals**; hydrogen sulphide, with salts of second group metals only. The precipitates are *sulphides*, except with chromium and aluminium; reduction occurring with ferric and arsenic salts, which form ferrous and arsenious sulphides. The precipitates have strongly marked **colors**—that of zinc being *white*; those of iron, copper, and lead, *black*; arsenic, *yellow*; antimony, *orange-red*; mercury, successively white, yellow, orange, and *black*.

668. Solutions of **nitro-ferricyanides** (633) give, with soluble metallic sulphides (or with hydrosulphuric acid after addition of an alkali, or with free sulphur after digesting with an alkali), an intense, rich *purple color*, disappearing after some time. Add a drop of the reagent, to a few drops of the solution, on a white porcelain surface. Vapors are tested for hydrosulphuric acid by conducting them into ammoniacal solution of sodium nitroferricyanide. (Vapors are tested for ammonia by passing them into solution of nitroferricyanide with hydrosulphuric acid.)

669. By ignition in the air, sulphur gives its characteristic odor of *sulphurous anhy-*

dride (682). Many of the *sulphides* yield more or less sulphurous anhydride; most of them are also, partly or wholly, converted to sulphates.

When ignited on **charcoal with sodium carbonate**—or (*distinction from sulphates*) *if ignited in a porcelain crucible* with sodium carbonate—soluble *sodium sulphides* are obtained. The production of the sodium sulphide is proved by the *black stain* of Ag_2S, formed on metallic **silver** by a moistened portion of the fused mass. (Compounds of selenium and tellurium, 499.)

SULPHURIC ACID.

670. Sulphuric anhydride, SO_3, is a colorless, fibrous, or waxy solid, melting (when recent) at 25° C. (77° F.), boiling at 46° C. (115° F.), and vaporizing with heavy white fumes in the air at ordinary temperatures. It is very deliquescent, and on contact with water combines rapidly, forming sulphuric acid and much heat.

671. Absolute sulphuric acid, H_2SO_4, is a colorless syrupy liquid; boiling at 338° C. (640° F.) At temperatures above about 160° C. (320° F.), it vaporizes from open vessels, slightly or abundantly, the vapors being white, heavy and suffocating, exciting coughing without giving premonition by odor. At ordinary temperatures it is strictly non-volatile and inodorous.

672. It is miscible with **water** in all proportions with production of heat; it abstracts water from the air (use in desiccators); and quickly abstracts the elements of water from many **organic compounds,** and leaves their *carbon,* a characteristic charring effect. It dissolves in alcohol, without decomposing it —but if in sufficient proportion producing ethylsulphuric acid, $HC_2H_5SO_4$.

673. Sulphuric acid *transposes the salts of nearly all other acids,* forming sulphates, and, either acids (as hydrochloric acid, 505), or the products of their decomposition (as with chloric acid, 520). But salts of mercury, silver, tin, and antimony, are with difficulty transposed by sulphuric acid. Also, *at temperatures above* about 300° C. (or 600° F.), phosphoric and silicic acids (and other acids not volatile at this temperature) transpose sulphates, with vaporization of sulphuric acid (compare 20).

674. Sulphuric acid dissolves most **metals**; though not quite so generally efficient for this purpose as hydrochloric or nitric acid. *Diluted sulphuric acid,* when cold, *dissolves—with evolution of hydrogen*—**magnesium, aluminium, zinc, iron, manganese,** and **tin**; and when heated, nickel, cobalt, and cadmium (*a*). *Concentrated sulphuric acid,* by application of heat, *dissolves —with evolution of sulphurous anhydride*—**copper, mercury, silver, bismuth,** and tin (*b*). (Compare 679.)

a. $Fe + H_2SO_4 = FeSO_4 + 2H$

b. $Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$

675. The metallic **Sulphates** are freely **soluble in water,** except those of *barium, lead, strontium* (very slightly soluble), and *calcium* (sparingly soluble). For specifications of the solubilities of the sulphates of barium, stron-

tium, and calcium, see 77; of lead, see 312. *Silver* sulphate requires about 200 parts of cold or 100 parts of hot water for solution, and mercurous sulphate is even more sparingly soluble. Bismuth, antimonious, and mercuric sulphates are soluble in acidulated water, but decomposed by pure water. The metallic sulphates are insoluble in alcohol (ammonium sulphate sparingly soluble in ordinary alcohol, very slightly in absolute alcohol).

In **analysis**, barium sulphate is chiefly obtained (676, 703). Alcohol is useful for separation of free sulphuric acid from its salts (678).

Acid sulphates of the alkali bases are formed as crystallizable salts. That of potassium, $KHSO_4$, gives off sulphuric acid above about 200° C. (400° F.); or by greatly diluting its solutions. That of sodium, $NaHSO_4$, is decomposed at a lower temperature, and hardly exists at all in solution. **Alcohol,** added to solutions of the acid sulphates, precipitates the normal sulphates, sulphuric acid remaining in solution:

$$2KHSO_4 = K_2SO_4 + H_2SO_4$$

676. Sulphuric acid, or solutions of sulphates, on addition of solutions of **barium salts,** as $BaCl_2$, or $Ba(NO_3)_2$, give a white precipitate of *barium sulphate,* $BaSO_4$; insoluble by hydrochloric or nitric acid. This insolubility is a *distinction from all acids,* except selenic and hydrofluosilicic. The precipitate, formed in cold solution, is so fine as to be difficult of removal by filtration; if formed in hot solution and then boiled, it is retained by a good filter. The full completion of the precipitate requires that the mixture should stand some time. In strongly acid solutions, a precipitate of $BaCl_2$, etc., may be obtained (see 84). A residue of sulphur may appear in this test, applied to thiosulphates (699). Solutions of **lead salts** give a white precipitate of *lead sulphate,* $PbSO_4$; not transposed with acids, soluble in solution of potassium hydrate. In solutions not dilute, **calcium salts** give a white precipitate of *calcium sulphate,* $CaSO_4$.

677. Alcohol precipitates the sulphates from their moderately concentrated water solutions; and its addition enables calcium chloride to precipitate the sulphate of calcium in very dilute solutions.

The sulphates insoluble in water are decomposed for analysis—(1st) by long boiling with solution of **alkali carbonate**; and more readily (2d) by fusion with an alkali carbonate. In both cases, there are produced—alkali *sulphates* soluble in water, and *carbonates* soluble by hydrochloric or nitric acid, *after* removing the sulphate (*a*). If the fusion be done on charcoal, more or less deoxidation will occur, reducing a part or the whole of the sulphate to sulphide (679), and the carbonate to metal (as with lead, 322), or leaving the metal as a carbonate or oxide (652).

a. $BaSO_4 + Na_2CO_3 = Na_2SO_4$ (soluble in water) $+ BaCO_3$ (soluble in acid).

678. Free sulphuric acid may be separated from sulphates (except ammonium sulphate) by strong alcohol, solutions being first evaporated nearly to dryness on the water bath.—A test for free *sulphuric acid, in distinction from sulphates,* may be made (in accordance with 672), by the use of **cane sugar,** as follows: A little of the liquid to be

tested is concentrated on the water-bath; then from two to four drops of it are taken on a piece of porcelain, with a small fragment of white sugar, and evaporated to dryness by the water-bath. A greenish-*black* residue indicates sulphuric acid. (With the same treatment, hydrochloric acid gives a brownish-black, and nitric acid, a yellow-brown residue.) A strip of white glazed paper, wet with the liquid tested, by immersing it several times at short intervals, then dried in the oven at 100° C., will be colored black, brown, or reddish, if the liquid contains as much as 0.2 per cent. of sulphuric acid.

679. Sulphuric acid and its salts are very stable at ordinary temperatures. They do not at all act as reducing agents—solution of permanganate not being decolored by sulphuric acid; but at *high temperatures*, they are able to act as **Oxidizing Agents** to some extent. (Further, see 819.) In the action of **metals** on hot concentrated sulphuric acid, there are cases of reduction of the sulphuric to *sulphurous acid*, as stated in 674 *b*; and in the action of **ignited carbon**, we have reduction of sulphates to *sulphides*, in fusion on charcoal, as follows:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$

680. It will be observed—sulphates **fused** *with sodium carbonate on charcoal*, leave a mass which contains sulphides, and, when moistened, stains **metallic silver** (as stated in 669); but, when fused with sodium carbonate (on porcelain) *without reducing agents*, leave a mass which, when moistened, *does not stain metallic silver* (distinction from sulphides).

681. By **heat alone**, the sulphates of the metals of the alkalies and alkaline earths, and of lead, are not decomposed. Other sulphates suffer dissociation—some giving off sulphuric anhydride; others, sulphurous anhydride and oxygen:

$$2FeSO_4 = Fe_2O_3 + SO_3 + SO_2$$
$$CuSO_4 = CuO + SO_2 + O$$

SULPHUROUS ACID.

682. **Sulphurous anhydride**, SO_2, is a colorless liquefiable **gas**, of a powerful, characteristic, suffocating odor and effect, that of burning sulphur. It bleaches litmus-paper. It is not combustible in the air. It dissolves readily in water, doubtless as sulphurous acid; the solution saturated at 15° C. (60° F.), containing about 14 per cent. of the sulphur dioxide; an increase of temperature greatly decreasing its solubility.

683. Absolute sulphurous acid, H_2SO_3, is a solid at 0° C. (32° F.), resolved into H_2O and SO_2 at temperatures much above the freezing point; but freely liquefiable with water at higher temperatures, as stated in the preceding paragraph. It may be supposed that the solution, at ordinary temperatures, is a mixture of water and H_2SO_3—a view resting on somewhat stronger support than we have for considering the solution of carbonic anhydride to contain H_2CO_3.

684. **Solution of Sulphurous Acid** first reddens litmus, and then bleaches it. It decomposes carbonates with effervescence. It has a strong odor from vaporization of sulphurous anhydride, which is soon completely expelled on boiling. By exposure to air it is gradually oxidized to sulphuric acid, from which it is seldom entirely free (691).

685. **The Sulphites** of the metals of the alkalies are freely soluble in water; the normal sulphites of all other metals are insoluble, or but very

slightly soluble in water. The sulphites of the metals of the alkaline earths, and some others, are soluble in solution of sulphurous acid—the solution being precipitated on boiling. The alkali bases form acid sulphites ("bisulphites"), which can be obtained in the solid state, but evolve sulphurous anhydride. The sulphites are insoluble in alcohol.

In **analysis**, sulphites are recognized by the odor of the anhydride, liberated by adding an acid (682). Also, by the reducing power (691) and by oxidation to sulphate (690). Further as to separation, see 703.

686. Solution of sulphurous acid (free from sulphuric acid) is but slightly precipitated by solutions of salts—owing to the solubility of sulphites in acids. See 19.

Sulphites are decomposed by all acids; except carbonic and boracic, and, in some instances, hydrosulphuric.

687. *Solutions of metallic sulphites are precipitated by the soluble* salts of all metals except those of the alkalies. The precipitates, mostly white, are soluble in acetic acid; also, except those of the first group metals, in hydrochloric acid, and, so far as not oxidized to sulphates, in dilute nitric acid. But these precipitated sulphites are almost invariably *accompanied by sulphates which are left undissolved by acids.*

688. Solution of **lead acetate** precipitates, from solutions of sulphites, *lead sulphite*, $PbSO_3$, white, easily soluble in dilute nitric acid; and not blackening when boiled (distinction from thiosulphate). Solution of **silver nitrate** gives a white precipitate of *silver sulphite*, Ag_2SO_3, easily soluble in very dilute nitric acid or in excess of alkaline sulphite, and turning dark-brown when boiled, by formation of metallic silver and sulphuric acid. Solution of **mercuric chloride** produces no change in the cold; but on boiling, the white *mercurous chloride* is precipitated, with formation of sulphuric acid. Still further digestion, with sufficient sulphite, reduces the white mercurous chloride to gray metallic mercury (equation 362 *b*).

689. Solution of **ferric chloride** gives a *red solution of ferric sulphite*, $Fe_2(SO_3)_3$; or, in more concentrated solutions, a *yellowish precipitate* of basic ferric sulphite, also formed by addition of alcohol to the red solution. The red solution is decolored on boiling; the acid radical reducing the basic radical, and forming ferrous sulphate.

690. Solution of **barium chloride** gives a white precipitate of *barium sulphite*, $BaSO_3$, easily soluble in dilute hydrochloric acid—*distinction from sulphate*, which is undissolved, and should be filtered out. Now, on adding to the filtrate **nitrohydrochloric acid,** a precipitate of barium sulphate is obtained—evidence that sulphite has been dissolved by the hydrochloric acid:

$$BaSO_3 + 2HCl_2 = BaCl_2 + H_2SO_3$$

$$BaCl_2 + H_2SO_3 + 2Cl + H_2O = BaSO_4 + 4HCl$$

691. Sulphurous acid and sulphites are active **Reducing Agents**, by virtue

of their *capacity for oxidation to sulphuric acid and sulphates.* See Oxidations, 818. Reduction by sulphurous acid is exemplified in the precipitations, given above, with silver and mercury, and with barium. Equations for other reductions are given, for ferric salts, 171 *b*; for chromic acid, 166 *c*; for iodine decoloration, 554 *c*; and for iodic acid, 571 *a* and *b*.

692. The reaction with iodic acid is employed as a test for sulphurous acid (as well as for iodic). A mixture of **iodic acid and starch** is turned violet to blue by traces of sulphurous acid or sulphites in vapor or in solution; the color being destroyed by excess of the sulphurous acid or the sulphite.

693. Notwithstanding this ready capacity for oxidation, sulphurous acid is capable of furnishing oxygen, though its power in the latter office is narrowly limited. As an **Oxidizing Agent**, sulphurous acid changes **stannous chloride** to stannic sulphide (*a*); reacts with the nascent hydrogen furnished by **zinc and dilute hydrochloric acid** to form water and *hydrosulphuric acid* (*b*); and with **zinc** alone (without other acid) dissolves the metal as *thiosulphate* without evolution of gas (*c*).

a. $H_2SO_3 + 3SnCl_2 + 6HCl = 3SnCl_4 + H_2S + 3H_2O$

$SnCl_4 + 2H_2S = SnS_2 + 4HCl$

b. $H_2SO_3 + 3Zn + 6HCl = 3ZnCl_2 + 3H_2O + H_2S$

c. $2Zn + 3H_2SO_3 = ZnS_2O_3 + ZnSO_3 + 3H_2O$

694. *Thiosulphates* are formed, also in reduction of sulphites, by continued boiling with **sulphur** (*a*), and in reduction of sulphurous acid with **metallic super-sulphides** in solution (*b*). Sulphurous acid with **hydrosulphuric acid**, both free, produce *pentathionic acid* (*c*), likewise a reduction of the sulphurous acid.

a. $Na_2SO_3 + S = Na_2S_2O_3$

b. $H_2SO_3 + Na_2S_2 = Na_2S_2O_3 + H_2S$

c. $5H_2SO_3 + 5H_2S = H_2S_5O_6 + 9H_2O + 5S$

695. By **heat alone**, sulphites either split into oxides and sulphurous anhydride (*a*), or into sulphates and sulphides (*b*).

a. $CaSO_3 = CaO + SO_2$

b. $4Na_2SO_3 = 3Na_2SO_4 + Na_2S$

696. Reactions of Effervescent Acids: Hydrosulphuric, Hydrocyanic, Carbonic, and Sulphurous.

Taken in Solution of their Potassium, Sodium, or other Soluble Salts.

	Sulphides.	Cyanides.	Carbonates.	Sulphites.
Salts of Second and Third Group bases, as Pb-$(C_2H_3O_2)_2$, Fe_2Cl_6.	*Precipitates: of Second Group*, formed by **H_2S**; *of Third Group*, by sulphides (136). See Table at 30.	Mostly *precipitates*, soluble in excess of the cyanide (616).	*Precipitates* of carbonates, basic carbonates or hydrates (651).	*Precipitates*, with most of these bases (687).
Salts of Fourth Group bases, as $CaCl_2$	No precipitates.	No precipitates.	*Precipitates.*	*Precipitates* (white).
Dilute Acids, H_2SO_4, HCl, HNO_3, or $HC_2H_3O_2$, to the concentrated solution or solid salt.	**H_2S**, *gas* (665).	**HCy**, *gas* (618).	**CO_2**, *gas* (649).	**SO_2**, *gas* (682).
$AgNO_3$ solution, to the gas.	**Ag_2S**, black (331).	**AgCy**, white (619).	No precipitate (648).	*Precipitate* (340).
$AgNO_3$, to the solution of salt.	" "	" "	**Ag_2CO_3**, white.	**Ag_2SO_3**, white (688).
NH_4OH, to the **Ag** precipitate.	Not dissolved.	Dissolved.	Dissolved.	Dissolved.
Ferric Chloride.	**S** and *ferrous sulphide* (186).	*Ferric hydrate* (189).	*Ferric hydrate* (185).	*Ferric sulphite*, red solution. On boiling, *ferrous* solution (171 *b*).
Permanganate.	Precipitate of **S**, loss of odor, reagent decolored.	Reagent decolored (625).	No change.	Loss of odor, reagent changes color.
Characteristic tests.	By fusion (669). By nitroprusside (668).	Forming sulphocyanate (622). " ferrocyanide (621).	. . . . .	By baric chloride and **HCl + Cl** (690).

THIOSULPHURIC ACID (HYPOSULPHUROUS ACID).

697. This acid, $H_2S_2O_3$, is hardly known in the free state. When its salts, the **Metallic Thiosulphates** (or "hyposulphites"), are decomposed by **acids**, the constituents of thiosulphuric acid are dissociated as sulphurous acid and sulphur. Nearly all acids in this way decompose thiosulphates:

$$Na_2S_2O_3 + 2HCl = 2NaCl + H_2SO_3 + S$$

The larger number of the thiosulphates (or hyposulphites) are **soluble in water**; those of barium, lead, and silver, being only very sparingly soluble. The thiosulphates are insoluble in alcohol. They are decomposed, but not fully dissolved, by acids, the decomposition leaving a residue of sulphur.

In **analysis**, thiosulphates are distinguished by giving a precipitate of sulphur with evolution of sulphurous anhydride when their solutions are treated with hydrochloric acid (700); by their intense reducing power (701), shown in the blackening of the silver precipitate (699); and by non-precipitation of calcium salts.

698. Alkali thiosulphate solutions dissolve the thiosulphates of lead, silver, and mercury; also, the chloride, bromide, and iodide of silver, and mercurous chloride; the iodide and sulphate of lead; the sulphate of calcium; and some other precipitates—by formation of soluble *double thiosulphates:*

$$Ag_2S_2O_3 + Na_2S_2O_3 = 2NaAgS_2O_3$$

Or:

$$Ag_2S_2O_3 + 2Na_2S_2O_3 = Na_4Ag_2(S_2O_3)_3$$

$$AgCl + Na_2S_2O_3 = NaAgS_2O_3 + NaCl$$

$$PbSO_4 + 3Na_2S_2O_3 = Na_4Pb(S_2O_3)_3 + Na_2SO_4$$

699. Barium chloride forms, in solutions of thiosulphates, a white precipitate of *barium thiosulphate*, BaS_2O_3, nearly insoluble in water; dissolving in acids, except the sulphur residue.—**Calcium chloride** forms no precipitate (distinction from sulphite).—Solutions of **silver nitrate** (339), **lead acetate**, and **mercurous nitrate**, form at first *white precipitates of thiosulphates*, soluble in excess of alkali thiosulphates, as stated in the preceding paragraph. These white precipitates, by standing, or quickly by warming, turn darker and finally *black, by formation of sulphides*, with sulphuric acid.

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$$

$$PbS_2O_3 + H_2O = PbS + H_2SO_4$$

Solution of copper salts, with thiosulphates, on long standing, precipitate cuprous salt, changed by boiling to sulphide and sulphuric acid, as above. For the precipitation of sulphides of **arsenic, antimony**, and, in the cold, **tin**, see 462.

700. The *precipitation of sulphur with evolution of sulphurous anhydride*, by addition of **dilute acids—as hydrochloric** or acetic—is characteristic of thiosulphates. It will be understood, however, that in pres-

ence of oxidizing agents, which can be brought into action by the acid, sulphides will likewise give a precipitate of sulphur (666).

701. Thiosulphates are **Reducing Agents**—even stronger and more active than the sulphites (691), to which they are so easily converted. This reducing power—or capacity for taking metalloids or acid radicals into combination—is exemplified by the conversion of **ferric salts** into ferrous salts (171 *c*), and by the bleaching of **iodine** solutions (554 *b*), both of which changes are so sharply defined that they are useful in volumetric analysis.

If the ferric solution be made red by addition of a few drops of sulphocyanate, the exact point of complete reduction is made obvious: while the inevitable color of free iodine is nearly sufficient to mark the point when loss of color shows that all the iodine has entered into combination, but the addition of starch-paste renders the indication more exact. In both these reactions, the oxidation of the thiosulphate changes it into a *tetrathionate*, as $Na_2S_4O_6$, or, in simpler terms, NaS_2O_3. Thus:

$$Cl + Na_2S_2O_3 = NaCl + NaS_2O_3$$

In other changes, sulphuric acid is formed. By greater or less degrees of oxidation, thiosulphates reduce chromic acid to chromic salts; permanganic acid, first to manganates (green), then to manganic salts; bromic and iodic acids first to bromine and iodine, and then, respectively, to hydrobromic and hydriodic acids; nitric acid to nitrogen oxides; and arsenic acid to arsenious compounds.

702. On **ignition**, or by heat short of ignition, all thiosulphates are decomposed. Those of the alkali metals leave sulphates and polysulphides (*a*), others yield sulphurous acid with sulphides, or sulphates, or both. The capacity of thiosulphates for rapid oxidation, renders their mixture with chlorates, nitrates, etc., *explosive*, in the dry way. **Chlorates** with hyposulphites, explode violently in the mortar (518). **Cyanides** and ferricyanides, fused with thiosulphates, form sulphocyanates, which may be dissolved by alcohol from other products.

a. $$4Na_2S_2O_3 = Na_2S_5 + 3Na_2SO_4$$

703. THE SEPARATION of the acids of **sulphur** from each other, in most instances, is effected without difficulty.

The insolubility of the barium precipitate in hydrochloric acid distinguishes and separates **sulphates** from sulphites and thiosulphates; the chlorine treatment (690), precipitating *both* the latter in the filtrate. The non-precipitation of thiosulphates by calcic chloride (699), distinguishes and separates them from sulphites; also, the precipitation of sulphur by hydrochloric acid (697) is a distinction.

Precipitation by excess of silver nitrate approximately separates sulphites and thiosulphates from **sulphates**; the solution of thiosulphate is distinguished by its redissolving the precipitate made by the first drop of silver nitrate solution (699), and by the subsequent blackening of the precipitate.

All compounds of sulphur, after **fusion** with sodium carbonate on charcoal, *give the black stain* on silver, 669. But of these compounds, only the *sul-*

phates fail to give the black stain after the fusion on porcelain in absence of a reducing agent, 680.

The test for **hydrosulphuric acid** by the vapor evolved under action of a stronger acid, cannot be relied upon in presence of sulphites or thiosulphates (694). But the immediately black precipitate with silver salt; the non-precipitation of alkaline earth metals, and the precipitation of sulphur by chlorine distinguish sulphides and thiosulphates.

704. PHOSPHORUS is an easily fusible and volatile solid, having a characteristic and disagreeable odor. It exists in different physical states or allotropic modifications, but it is invariably more or less rapidly oxidized in the air, though it does not decompose water. White phosphorus is luminous in the dark, and takes fire at a little above its melting point, 44° C. (111° F.); red phosphorus takes fire at 260° C. (500° F.) The product is chiefly phosphoric anhydride, but some phosphorous anhydride is formed.

705. When phosphorus is digested in warm solution of **hydrate of potassium or sodium** or in a mixture of **lime** and water, three-fourths of the phosphorus dissolves as hypophosphite (KH_2PO_2), and one-fourth vaporizes as phosphorous hydride, PH_3, each bubble of which takes fire as it enters the air. Thus:

$$3NaOH + 4P + 3H_2O = 3NaH_2PO_2 + PH_3$$

$$3Ca(OH)_2 + 8P + 6H_2O = 3CaH_4(PO_2)_2 + 2PH_3$$

Phosphorus is oxidized to orthophosphoric acid, slowly but completely, by digestion with **nitric acid**, chlorine, or bromine, with water. In this manner the unoxidized phosphorus of iron ores, cast iron, and of organic bodies, is determined; and this is one method of preparing pharmacopœial diluted phosphoric acid. Phosphorus acts vigorously as a **reducing agent**, but in most conditions with less power than the metals of the alkalies and alkaline earths. Vapor of phosphorus blackens solution of **silver nitrate**: a delicate test made by digesting the material at 30° to 40° C., the vessel being covered with paper wet with the reagent. The blackened paper is tested for phosphoric acid.

Phosphorus stands between nitrogen and arsenic, in the relations of the Nitrogen Series, 584.

The most important **Acids of Phosphorus** are:

Phosphoric acid,	orthophosphoric,	$H_3P^vO_4$,	corresponding to $3H_2O.P_2O_5$.
	pyrophosphoric,	$H_4P_2O_7$,	" $2H_2O.P_2O_5$.
	metaphosphoric,	HPO_3,	" $H_2O.P_2O_5$.
Hypophosphorous acid,		$H_3P'O_2$,	" $3H_2O.P_2O$.

PHOSPHORIC ACID.

706. Phosphoric anhydride, P_2O_5, is a white, amorphous solid, fusible at a high temperature, and slowly volatile at a white heat without decomposition. It is deliquescent, combining with water with excessive avidity, and forming metaphosphoric acid, monobasic. The latter is not dehydrated by heat alone.

707. Orthophosphoric acid, H_3PO_4, is a translucent, feebly crystallizable, and very deliquescent soft solid; reduced by heat first to pyrophosphoric acid, then to metaphosphoric acid, which is nearly non-volatile.

Orthophosphoric acid is formed from phosphorus by oxidation in water, as stated in 705; and from metaphosphoric acid or pyrophosphoric acid by digesting with dilute mineral acids, or even by long boiling in water, or, as sodium salt, by fusion with excess of sodium carbonate.

Phosphoric acid is formed from metallic phosphates by transposition with acids in cases where a precipitate results, as a lead or barium phosphate with sulphuric acid, or silver phosphate with hydrochloric acid—19 (2). But when the products are all soluble, as calcium phosphate with acetic acid or sodium phosphate with sulphuric acid, the transposition is only partial; so that unmixed phosphoric acid is not obtained. A non-volatile acid like phosphoric, is not separated from liquid mixtures, as the volatile acids are, like hydrochloric. The change represented by equation (*a*) can be so verified that pure phosphoric acid will be separated, but the changes shown in equations (*b*) and (*c*) do not comprise the whole of the material taken. In the operation (*b*), some sodium phosphate and some nitric acid will be left, and in (*c*) some trihydrogen phosphate will no doubt be made.

a. $CaH_4(PO_4)_2 + H_2C_2O_4 = CaC_2O_4 + 2H_3PO_4$

b. $Na_2HPO_4 + 2HNO_3 = 2NaNO_3 + H_3PO_4$

And $Na_2HPO_4 + HNO_3 = NaNO_3 + NaH_2PO_4$

c. $2CaHPO_4 + 2HCl = CaCl_2 + CaH_4(PO_4)_2$

708. The **Orthophosphates,** *dimetallic and trimetallic,* are **insoluble in water**—except those of the metals of the ordinary alkalies. They are all, however, more or less soluble in aqueous phosphoric acid by formation of *monometallic* salts, as $CaH_4(PO_4)_2$, having an acid reaction. Lithium phosphate is nearly insoluble in water. Phosphates are insoluble in alcohol.

In **analysis,** the molybdate precipitate (714) is most distinctive. Separation by the ferric phosphate precipitate in presence of acetic acid (247) is employed. Separation from oxalate, as calcium precipitate, by acetic acid, is used in systematic qualitative work (710 and 801). Ignition test: see 717.

709. Soluble salts of all metals, except those of the alkalies, precipitate solutions of ordinary phosphates (dimetallic and trimetallic orthophosphates).

710. Soluble salts of the alkaline earth metals, with **dimetallic** alkali phosphates, as Na_2HPO_4, form white precipitates of *phosphates, two-thirds metallic,* as $CaHPO_4$; with **trimetallic** alkali phosphates, white precipitates of *phosphates, normal* or full metallic, as $Ca_3(PO_4)_2$. The precipitates are soluble in acetic acid, and in the stronger acids (707 *c*). Concerning the ammonium magnesium phosphate, see 117.

711. Solutions of orthophosphates give, with soluble ferric, chromic, and aluminium salts, mostly the normal *phosphates,* $Fe_2(PO_4)_2$, etc. The *ferric phosphate* is but slightly soluble in acetic acid, and for this reason it is made the *means of separating phosphoric acid from metals* of the earths and alkaline

earths (247). Solution of sodium or potassium acetate is added; and if the reaction is not markedly acid, it is made so by addition of Acetic Acid. Ferric chloride (if not present) is now added, drop by drop, avoiding an excess. The precipitate, *ferric phosphate*, is brownish-white.

With zinc and manganous salts, the precipitate is dimetallic or normal—$ZnHPO_4$, or $Zn_3(PO_4)_2$—according to the conditions of precipitation. Manganic salts give a colored solution, as explained in 214. With salts of nickel, a light green normal phosphate is formed; with cobalt, a reddish normal phosphate.

712. Silver salts precipitate normal *silver phosphate*, Ag_3PO_4, light yellow, soluble in acetic and nitric acids and in ammonium hydrate. The *color of the silver precipitate* distinguishes ortho- from pyro-phosphoric acid. Lead salts precipitate mostly $Pb_3(PO_4)_2$, but slightly soluble in acetic acid. Bismuth salts form $BiPO_4$, peculiar in being insoluble in dilute nitric acid. Copper forms a bluish-white precipitate, either normal or two-thirds metallic. Mercurous salts precipitate *mercurous phosphate*, $Hg_6(PO_4)_2$, white. Mercuric nitrate (not the chloride) precipitates mercuric phosphate, $Hg_3(PO_4)_2$, white.

713. If a disodium or dipotassium orthophosphate is added to solution of silver nitrate, free acid is formed, and an acid reaction to test-paper is induced (*a*). But with a trisodium or tripotassium phosphate, the solution remains neutral (*b*)—a *means of distinguishing the acid phosphates from the normal.*

a. $3Na_2HPO_4 + 6AgNO_3 = 2Ag_3PO_4 + H_3PO_4 + 6NaNO_3$

b. $Na_3PO_4 + 3AgNO_3 = Ag_3PO_4 + 3NaNO_3$

714. **Ammonium Molybdate**, in its nitric acid solution (494), furnishes an exceedingly delicate test for phosphoric acid, giving the pale yellow precipitate, termed *ammonium phosphomolybdate.* The molybdate should be in excess, therefore it is better to add a little of the solution tested (which must be neutral or acid) to the reagent, taking a half to one cub. cent. of the latter in a test-tube. For the full delicacy of the test, it should be set aside, at 30° to 40° C., for several hours.

715. **Free** orthophosphoric acid is not precipitated by ordinary salts of third and fourth group metals (in instance of ferric chloride, a distinction from pyrophosphoric acid and metaphosphoric acid),* but is precipitated in part by

* A solution containing 5 p. c. *ferric chloride*, mixed with one-fourth its volume of a 10 p. c. solution of *orthophosphoric* acid, requires that near half of the latter be neutralized (so that phosphate is to phosphoric acid as 1.114 is to 1.000) before precipitation occurs. On the other hand 4 c. c. of a 5 p. c. solution of ferric chloride, mixed with 1 c. c. of a 6 p. c. solution of *metaphosphoric* acid, form a precipitate, to dissolve which 20 c. c. of the same metaphosphoric acid solution or 5 c. c. of a 24 p. c. solution of hydrochloric acid are required. Four c. c. of a 5 p. c. solution of *silver nitrate* with 1 c. c. of a 10 p. c. solution of *orthophosphoric* acid give a precipitate, to dissolve which requires 7 c. c. of the same orthophosphoric acid solution. [The Author's report of work by Mr. Morgan, *Am. Jour. Phar.*, xlviii. (1876), 534.]

silver nitrate, and lead nitrate and acetate. **Ammoniacal solution of calcium chloride** or of barium chloride precipitates free orthophosphoric acid.

716. Orthophosphoric acid—or an orthophosphate with acetic acid—*does not coagulate* egg **albumen** or **gelatine**. This is a distinction of both orthophosphoric acid and pyrophosphoric acid *from metaphosphoric acid.*

717. **Ignition with metallic magnesium** (or sodium) reduces phosphorus from phosphates to magnesium *phosphide*, recognized by odor of PH_3, formed on contact of the phosphide with water. A bit of magnesium wire (or of sodium) is covered with the previously ignited and powdered substance in a glass tube of the thickness of a straw, and heated. If any combination of phosphoric acid is present, vivid incandescence will occur, and a black mass will be left. The latter, crushed and wet with water, gives the odor of phosphorous hydride.

718. **PYROPHOSPHATES** are precipitated from their solutions by **silver nitrate**, as *silver pyrophosphate*, $Ag_4P_2O_7$, *white*, soluble in ammonium hydrate and in nitric acid.

The *pyrophosphates of the alkaline earth metals* are difficultly soluble in **acetic acid.** The most of the pyrophosphates of the heavy metals, except silver, are soluble in solutions of alkali pyrophosphates, as *double pyrophosphates soluble* in water (distinctions from orthophosphates).

Ammonium molybdate reacts but slowly with pyrophosphate solutions—and not until orthophosphate is *formed by digestion with the nitric acid* of the reagent solution.

Magnesium salts with ammonium hydrate give a precipitate of double *pyrophosphate*, soluble in alkali pyrophosphate solution.

Free pyrophosphoric acid gives precipitates with solutions of silver nitrate, lead nitrate or acetate, and ferric chloride; no precipitates with barium or calcium chloride, or with magnesium or ferrous sulphate. (Further, see 715.)

719. **METAPHOSPHATES** are especially distinguished, by the means mentioned in 715 and 716. Also, they are not precipitated by solutions of magnesium salts with ammonium hydrate, unless very concentrated, or by the molybdate solution. The *silver precipitate*, $AgPO_3$, *white*, is soluble in alkali metaphosphate solutions, distinction from pyrophosphates.

Free metaphosphoric acid precipitates solutions of silver nitrate, lead nitrate, and lead acetate, the precipitates being insoluble in excess of metaphosphoric acid, and soluble in moderately dilute nitric acid. Barium, calcium, and ferrous chlorides, and magnesium, aluminium and ferrous sulphates, are not precipitated by free metaphosphoric acid. Ferric chloride is precipitated, a distinction from orthophosphoric acid. See 715.

There are various polymeric modifications of metaphosphoric acid, distinguished from each other chiefly by physical differences of the acids and their salts. Pure metaphosphoric acid is a white, viscid, or waxy solid. (Ordinary glacial phosphoric acid owes its hardness to the universal presence of sodium metaphosphate.)

Fusion with excess of sodium carbonate converts both metaphosphates and pyrophosphates to normal orthophosphate.

720. Reactions of Sulphuric, Phosphoric, and Oxalic Acids.

As Acids.	H_2SO_4.	H_3PO_4	$H_2C_2O_4$
	Vaporizes at 640° F.	*Vaporizes slowly when ignited.*	*Vaporizes with decomposition at about* 330° F.
	Precipitates the same as metallic sulphates.	*Does not precipitate salts of the stronger acids* (715).	*Precipitates chlorides, nitrates, and sulphates, only partly or not at all. Precipitates acetates,* 19.
	Chars organic matter (672).	*Not caustic.*	*Not caustic, but poisonous.*
As Metallic Salts: (Compare 30.)	**Sulphates.**	**Phosphates.**	**Oxalates.**
	Precipitate **Pb, Ba, Sr,** *and* **Ca,** (676).	*Precipitate non-alkali salts* (708).	*Precipitate most non-alkali salts* (656).
Precipitations most used in analysis:	$BaSO_4$ $PbSO_4$	$MgNH_4PO_4$ (117). $Fe_2(PO_4)_2$ (711). $CaHPO_4$ or $Ca_3(PO_4)_2$.	CaC_2O_4 (107). $Ag_2C_2O_4$ (658 *c*).
Precipitates:	Not dissolved by acids.	Dissolved by **acetic acid,** except **Fe,** etc. (247).	Transposed by **hydrochloric,** not by acetic acid (655).
Fused with Na_2CO_3 on charcoal:	First Na_2SO_4, then Na_2S (680).	(Na_3PO_4).	*Carbonates.*
H_2SO_4, concentrated, with heat:	. . . . .	. . . . .	Effervescence of CO_2+CO (653).
$KMnO_4$ . . .	. . . . .	. . . . .	Reduced.
$K_2Cr_2O_7 + H_2SO_4$	. . . . .	. . . . .	Reduced.

HYPOPHOSPHOROUS ACID.

721. Absolute hypophosphorous acid, H_3PO_2, is a colorless, viscid liquid; miscible with water, and gradually oxidizing in the air to phosphoric and phosphorous acids. It reduces silver and mercury from their salts. It is reduced by hydrogen, as generated by zinc and sulphuric acid, to phosphorous hydride, PH_3.

722. **Hypophosphites** are prepared according to 705. They are transposed by most of the ordinary acids, but if nitric acid be employed, oxidized products of hypophosphorous acid are obtained. Even sulphuric acid oxidizes hypophosphorous acid to some extent.

723. The hypophosphites are all **soluble in water.** Alcohol dissolves the hypophosphites of the alkali metals, not those of the alkaline earth metals.

For **identification,** the ignition test (725), is among the most characteristic.

724. Although hypophosphites are not precipitable by transposition, they cause numerous precipitates by **Reduction,** eagerly taking oxygen (or other electro-negatives in presence of water) to form phosphates. Mercuric chloride gives first a white precipitate of *mercurous chloride,* then a gray one of *mercury.* Silver nitrate gives a brown-black precipitate of *silver,* white before complete reduction. The reactions of hypophosphites as reducing agents are given in 816. With copper salts, the reduction of metallic *copper* is effected by boiling in strong solution of potassium or sodium hydrate, *phosphite* being first and chiefly formed, so that this is a distinction of hypophosphites from phosphites. By boiling in a concentrated solution of **potassium hydrate,** hypophosphites decompose water, liberating *hydrogen* and forming phosphates. In this test, a piece of solid potassium hydrate is added. With solution of barium hydrate, the formation of free hydrogen proceeds slowly, and some phosphite is produced. The reaction of **zinc and dilute sulphuric acid** (721), giving phosphorous hydride in Marsh's apparatus, is characteristic for *hypophosphites and phosphites.* Hypophosphites are *distinguished from phosphites*—by giving no precipitates in solutions of baric or calcic salts (non-alkali phosphites being mostly insoluble in water), also by reducing copper in a boiling solution of cupric sulphate.

725. On **ignition,** hypophosphites decompose with explosive deflagration of phosphorous hydride, and formation of pyrophosphates:

$$2CaH_4(PO_2)_2 = Ca_2P_2O_7 + H_2O + 2PH_3$$

BORIC OR BORACIC ACID.

726. **BORON** is an infusible, non-volatile solid, existing in different allotropic conditions. Amorphous boron takes fire at about 300° C., and burns in the air to *boracic anhydride,* B'''_2O_3, the only known oxide of boron. Boron is not obtained in the elemental state by ordinary analytical operations.

727. Boric anhydride, B_2O_3, forms several acids, that obtained in crystals being

trihydric, H_3BO_3, known as orthoboric acid. At 100° C., this is converted to metaboric acid, HBO_2. Ignition of the acid leaves the vitreous anhydride. Numerous polymeric metaborates are known. Both anhydride and acid are soluble in water and in alcohol. These solutions redden litmus, and turn turmeric paper brownish-red—this color becoming intense when the paper is dried.

728. The **Borates** of the metals of the alkalies are **soluble in water**; those of the other metals are insoluble in water, but in general are made soluble by free boric acid. They are all nearly or quite insoluble in alcohol. Borates are identified especially by the green color they impart to flames (730, 733).

729. **Silver nitrate** forms, in solutions of acid borates, a white precipitate of *silver borate*, $AgBO_2$, but normal borates form in part silver oxide, brown. **Lead acetate** gives a white precipitate of *lead borate*, $Pb(BO_2)_2$; **calcium chloride**, in solutions not very dilute, a white precipitate of *calcium borate*; and **barium chloride**, in solutions not dilute, a white precipitate of *barium borate*, $Ba(BO_2)_2$. With **aluminium** salts, the precipitate is *aluminium hydrate*.

730. Borates are transposed with formation of boracic acid, by all ordinary acids—in some conditions even by carbonic acid; the transposition being partial when soluble products result, as with phosphoric acid, 707.

The liberated boracic acid is dissolved by **alcohol**, and if the alcohol solution be set on fire, it burns with a *green flame*.

731. A solution of a borate, acidulated with hydrochloric acid to a barely perceptible acid reaction, imparts to a slip of **turmeric paper** half wet with it, a dark-red color, which on drying intensifies to a characteristic *red color*.

732. The reaction given in 748 may be employed as a test, **in the dry way**, for boron—taking **calcium fluoride** as a reagent.

Borates fused in the *inner blow-pipe flame* with potassium acid sulphate give *the green color* to the outer flame.

If a crystal of boric acid, or a solid residue of borate previously treated with sulphuric acid, on a porcelain surface, is played upon by the flame of Bunsen's Burner, the green flame of boron is obtained.

733. If a powdered borate (previously calcined), is moistened with sulphuric acid and heated on platinum wire to expel the acid, then moistened with **glycerine** and burned; the green flame appears with great distinctness.*

The glycerine is only ignited, then allowed to burn by itself. Barium does not interfere (being held as sulphate, non-volatile); copper should be previously removed in the wet way. The glycerine flame gives the spectrum. But in all flame tests, boric acid must be liberated.

734. Borates (fused on platinum wire with sodium carbonate) give a characteristic spectrum of four lines, equidistant from each other, and extending from **Ba** γ in the green to **Sr** δ in the blue.

* M. W. Iles, *American Chemist* (1876), p. 361.

SILICIC ACID.

735. Silicon is a solid, existing in different allotropic states; difficultly fusible, and more or less easily oxidizable by the air at high temperatures, or by oxidizing solvents, to silicic anhydride or acid. The latter is not deoxidized by any ordinary blow-pipe operations.

736. Silicic Anhydride, or silica, $Si''''O_2$, is a stable, non-volatile, infusible solid; insoluble in water or acids, soluble in fixed alkali hydrate solutions, by formation of silicates. These are formed as normal salts, quadribasic; metasalts, dibasic; and in many other proportions of base and acid.

$$SiO_2 + 4KOH = K_4SiO_4 + 2H_2O$$

737. Of the **Silicates**, only those of potassium and sodium are **soluble** in water. The solutions of alkali silicates somewhat resemble, in the nature of their union, the alkaline solutions of zinc, aluminium, and lead. These silicates in solution are decomposed by all acids, including carbonic, with separation of silicic acid, H_4SiO_4, gelatinous. Silicic acid is soluble, silicic anhydride insoluble, in the mineral acids. Some of the insoluble silicates are also dissolved by sulphuric and by hydrochloric acid, with separation of gelatinous silicic acid. Other silicates are dissolved by these acids, when heated in closed tubes at about 200° C. Soluble silicates precipitate, from salts of non-alkali metals, silicates insoluble in water, but mostly soluble in acids.

Silicates are **determined**, qualitatively or quantitatively, by the separation of the anhydride, 738.

738. Silicic acid is obtained as H_2SiO_3, H_4SiO_4, and other hydrates of SiO_2. It is decomposed by evaporation to dryness, with a residue of silica, insoluble in acids.—Hence, when an alkali silicate is *acidulated* (with hydrochloric or nitric acid), and *evaporated strictly to dryness* on the water-bath, and again treated with water and the same acid, the silica is left behind insoluble. This behavior is characteristic for silicic acid, and serves for its **separation** as well as detection.

The formation of the alkali silicate, from *silica or an insoluble silicate*, as the first step in this operation, is generally obtained in the dry way, by **fusion**, with three or four parts of mixed **carbonates of sodium and potassium** in a porcelain crucible. (These carbonates, mixed in about molecular proportions, fuse at a much lower temperature than either alone.)—Also, the soluble silicates may be formed by boiling with solution of potassium hydrate or sodium hydrate, as stated in 736; the operation being performed in a silver or platinum vessel. Silica dissolves, with more or less readiness, in boiling solution of potassium or sodium carbonate.

Silica is not soluble in **ammonium hydrate**, and the salts of ammonium separate gelatinous silica from solutions of potassium or sodium silicate.

Therefore, in operating with these solutions, silica is precipitated with the bases of the third group:

$$K_4SiO_4 + 4NH_4Cl + 4H_2O = H_4SiO_4 + 4KCl + 4NH_4OH$$

739. In the fused **bead** of microcosmic salt, particles of silica *swim undissolved.* If a silicate be taken, its base will, in most cases, be dissolved out, leaving a "*skeleton of silica*" undissolved in the liquid bead.—But with a bead of sodium carbonate, silica (and most silicates) fuse to a clear *glass* of silicate.

For the reactions of silica with fluorides, see 741.

740. Silica is separated from the fixed alkalies in natural silicates, by mixing the latter in fine powder with three parts of precipitated calcium carbonate, and one-half part of ammonium chloride, and heating in a platinum crucible to redness for half an hour, avoiding too high a heat. On digesting in hot water, the solution contains all the alkali metals, as chlorides, with calcium chloride and hydrate. [J. Lawrence Smith.]

741. FLUORINE, in several characteristics, appears as the first member of the Chlorine Series of Elements (500). It cannot be preserved in the elemental state, as it combines with the materials of vessels (except fluor-spar), and instantly decomposes water, forming *hydrofluoric acid*, **HF**, an acid prepared by acting on calcium fluoride with sulphuric acid (*a*). Fluorine also combines with silicon as SiF_4, *silicon fluoride*, a gaseous compound, prepared by acting on calcium fluoride and silicic anhydride with sulphuric acid (*b*). On passing silicon fluoride into water, a part of it is transposed with the water, forming silicic acid and hydrofluoric acid (*c*); but this hydrofluoric acid does not at all remain free, but combines with the other part of the fluoride of silicon, as *hydrofluosilicic acid*, $(HF)_2SiF_4$, or H_2SiF_6 (*d*). This acid is used as a reagent; forming metallic silico-fluorides, soluble and insoluble (749).

a. $CaF_2 + H_2SO_4 = CaSO_4 + 2HF$

b. $2CaF_2 + SiO_2 + 2H_2SO_4 = 2CaSO_4 + 2H_2O + SiF_4$

c. $SiF_4 + 2H_2O = SiO_2 + 4HF$ (not remaining free).

d. $2HF + SiF_4 = H_2SiF_6$

c. and d. $3SiF_4 + 2H_2O = SiO_2 + 2H_2SiF_6$

HYDROFLUORIC ACID.

742. A colorless, intensely corrosive gas, soluble in water to a liquid that reddens litmus, rapidly corrodes glass, porcelain, and the metals, except platinum and gold (lead but slightly). Both the solution and its vapor act on the flesh as an insidious and virulent caustic, giving little warning, and causing obstinate ulcers.

743. The **Fluorides** of the alkali metals are freely **soluble in water**, the solutions alkaline to litmus and slightly corrosive to glass; the fluorides of the alkaline earth metals are insoluble in water; of copper, lead, zinc, and ferricum, sparingly soluble; of silver

and mercury readily soluble. Fluorides are **identified** by the action of the acid upon glass (745).

744. Calcium chloride solution forms, in solution of fluorides or of hydrofluoric acid, a gelatinous and transparent precipitate of *calcium fluoride*, CaF_2, slightly soluble in cold hydrochloric or nitric acid and in ammonium chloride solution. **Barium chloride** precipitates, from free hydrofluoric acid less perfectly than from fluorides, the voluminous, white, *barium fluoride*, BaF_2. Silver nitrate gives no precipitate.

745. Sulphuric acid transposes with fluorides, forming *hydrofluoric acid*, **HF**, (741 *a*). The gas is distinguished from other substances by *etching hard glass*—previously prepared by coating imperviously with (melted) wax, and writing through the coat. The operation may be conducted in a small leaden tray, or cup formed of sheet lead: the pulverized fluoride being mixed with sulphuric acid to the consistence of paste.

746. If the fluoride be mixed with **silicic acid**, we have, instead of hydrofluoric acid, *silicon fluoride*, SiF_4 (741 *b*); a gas which does not attack glass, but when passed into water produces hydrofluosilicic acid, H_2SiF_6 (741 *c*, *d*) (749).*

747. Also, heated with acid sulphate of potassium, in the dry way, fluorides disengage hydrofluoric acid. If this operation be performed in a small test-tube, the surface of the glass above the material is corroded and roughened:

$$CaF_2 + 2KHSO_4 = CaSO_4 + K_2SO_4 + 2HF$$

748. By heating a mixture of borax, acid sulphate of potassium, and a fluoride, fused to a bead on the loop of platinum wire, in the clear flame of the Bunsen gas-lamp, an evanescent *yellowish-green color* is imparted to the flame.

749. HYDROFLUOSILICIC ACID, $(HF)_2SiF_4$, or H_2SiF_6, prepared as directed in the note to 746, forms metallic *silicofluorides*, mostly soluble in water; those of barium, sodium, and potassium, being only slightly soluble in water, and made quite insoluble by addition of alcohol (compare 92). The silicofluorides are precipitated translucent and gelatinous. With concentrated sulphuric acid, they disengage hydrofluoric acid, **HF**. By heat, they are resolved into fluorides and silicon fluoride: as, $BaF_2 + SiF_4$.

ACETIC ACID.

750. Absolute acetic acid, $H(C_2H_3O_2)$, is a transparent solid, melting at about 16° C. (61° F.), boiling at 119° C. (246° F.) It vaporizes gradually from its water solutions at ordinary temperatures; more rapidly as they are stronger, the vapor having the characteristic odor of vinegar.

751. The salts of acetic acid—the metallic **Acetates**—are all **soluble in water**; *argentic and mercurous acetates but sparingly soluble.* Most of the

* *Hydrofluosilicic acid* is directed to be prepared by taking one part each of fine sand and finely-powdered fluor-spar, with six to eight parts of concentrated sulphuric acid, in a small stoneware bottle or a glass flask, provided with a wide delivery-tube, dipping into a little mercury in a small porcelain capsule, which is set in a large beaker, containing six or eight parts of water. The stoneware bottle or flask is set in a small sand-bath, with the sand piled about it, as high as the material, and gently heated from a lamp. Each bubble of gas decomposes with deposition of gelatinous silicic hydrate. When the water is filled with this deposit, it may be separated by straining through cloth and again treating with the gas for greater concentration. The strained liquid is finally filtered and preserved for use.

acetates, except mercurous and silver acetates, dissolve in alcohol. They have a slight odor of the acid. For **identification**, the odor of the acid, and of its ether (754), and the color of the ferric solution (753), are employed. Ignition-tests, 756.

752. The stronger mineral acids transpose with acetates, forming acetic acid. Solid acetates, with concentrated sulphuric acid, evolve strong acetous vapor; but if the heat is somewhat increased, the mixture blackens from separation of carbon (672), and at higher temperatures sulphurous and carbonic anhydrides are evolved.

753. Solution of **ferric chloride** forms, with solutions of acetates, a *red solution* containing *ferric acetate*, $Fe_2(C_2H_3O_2)_6$, which on boiling precipitates brownish-red, basic ferric acetate. The red solution is not decolored by solution of mercuric chloride (distinction from sulphocyanate); but is decolored by strong acidulation with sulphuric acid or hydrochloric acid (distinction from sulphocyanate and from meconate). The ferric acetate is precipitated by alkali hydrates.

754. If acetic acid or an acetate is warmed with **sulphuric acid** and a *little* **alcohol**, the characteristic pungent and *fragrant odor of ethyl acetate* or acetic ether is obtained:

$$H(C_2H_3O_2) + C_2H_5OH = H_2O + C_2H_5(C_2H_3O_2)$$

755. Acetic acid does not act as a **Reducing Agent** as readily as do most of the organic carbon compounds. It reduces permanganates and chromates but slowly, even in boiling solution; reduces auric chloride only in alkaline solution, and does not reduce alkaline copper solution. It takes chlorine into combination—slowly in ordinary light, quickly in sunlight, forming chloracetic acids.

756. By **ignition** alone, acetates blacken, with evolution of vapor of *acetone*, C_3H_6O, inflammable and of an agreeable odor. By prolonged ignition of acetates in the air, carbonates are obtained free from charcoal.—By ignition with **alkali hydrates** in dry mixture, *marsh-gas*, CH_4, is evolved.—By ignition with **alkalies** and **arsenious anhydride**, the offensive vapor of cacodyl oxide is obtained (383).

TARTARIC ACID.

757. Tartaric acid, $H_2C_4H_4O_6$, is a colorless, crystallizable, non-volatile solid, freely soluble in water, and in alcohol. It may be separated from bases by adding sulphuric acid and alcohol.

The **Tartrates** of the alkali bases are **soluble in water**; the normal tartrates being freely soluble, the acid tartrates of potassium and ammonium sparingly soluble (41 and 61). The tartrates of the alkaline earth bases and of the non-alkali bases, are insoluble or sparingly soluble, but mostly dissolve

in solution of tartaric acid. Most of the tartrates are insoluble in alcohol. There are double tartrates of heavy metals with alkali metals, which dissolve in water.

Hydrochloric, nitric, and sulphuric **acids** transpose the tartrates (whether forming solutions or not). Most of the tartrates are also dissolved (and, if already dissolved, are not precipitated) by the **alkali hydrates**, owing to the formation of soluble double tartrates (133).

The potassium acid tartrate, precipitated with help of alcohol, and the silver reduction, are of greatest **analytical** interest.

758. Solution of **calcium hydrate**, added to alkaline reaction, precipitates from cold solution of tartaric acid, or of soluble tartrates, *calcium tartrate*, white, $Ca(C_4H_4O_6)$. Solution of calcium chloride with neutral tartrates, gives the same precipitate. Solution of calcium sulphate forms a precipitate but slowly, or not at all (distinction from racemic acid). The precipitate of calcium tartrate is soluble in cold solution of potassium hydrate, precipitated gelatinous on boiling, and again made soluble on cooling (distinctions from citrate), and dissolves in acetic acid (distinction from oxalate).

759. **Silver nitrate** precipitates, from solutions of normal tartrates, *silver tartrate*, $Ag_2(C_4H_4O_6)$, white, becoming black when boiled. If the precipitate is filtered, washed, dissolved from the filter by dilute ammonium hydrate into a clean test-tube, left for a quarter of an hour on the water-bath, the silver is reduced as a *mirror coating* on the glass (340), distinction from citric acid. Free tartaric acid does not reduce silver salts. **Permanganate** is **reduced** quickly by alkaline solution of tartrates (distinction from citrates), precipitating manganese dioxide, brown. Free tartaric acid acts but slowly on the permanganate. Alkaline copper tartrate resists reduction in boiling solution. **Chromates** are reduced by tartaric acid, the solution turning green. The oxidized products, both with permanganate and chromate, are formic acid, carbonic anhydride, and water.

760. On **ignition**, tartaric acid or tartrates evolve the *odor of burnt sugar*, *separating carbon*, and becoming finally converted to carbonates.—Strong **sulphuric acid** also blackens tartrates, on warming. Melted **potassium hydrate**, below ignition, produces acetate and oxalate.

CITRIC ACID.

761. Citric acid, $H_3(C_6H_5O_7)$, is a colorless, crystallizable, non-volatile solid; freely soluble in water and in alcohol.

The **Citrates** of the metals of the alkalies are freely **soluble in water**; those of iron and copper are moderately soluble; those of the alkaline earth metals insoluble. There are many soluble double citrates formed by action of alkali citrates upon precipitated citrates, or of alkali hydrates upon metallic salts in presence of citric acid: see 133. In **distinction** from tartrates, the solubility of the potassium salts (764); non-precipitation of calcium salt in cold solution; and weaker reducing action, are to be noted.

762. Solution of **calcium hydrate** in excess (as by dropping the solution tested into the reagent) gives no precipitate with citric acid or citrates in the cold (distinction from tartaric acid), but on heating, the white, *calcium citrate*, $Ca_3(C_6H_5O_7)_2$, is precipitated (not soluble in cold potassium hydrate solution). By filtering before boiling, the tartrate and citrate may be approximately separated. Calcium chloride also gives the same precipitate after boiling. Calcium citrate is soluble in acetic acid (distinction from oxalates).

763. Solution of **lead acetate** precipitates white, *lead citrate*, $Pb_3(C_6H_5O_7)_2$, soluble in ammonia. **Silver nitrate** gives a white precipitate of *silver citrate*, $Ag_3(C_6H_5O_7)$, which does not blacken on boiling (distinction from tartrate).

764. One part of citric acid dissolved in two parts of water, and treated with a solution of one part of potassium acetate in two parts of water, should remain clear *after* addition of an equal volume of strong alcohol (absence of oxalic acid and of tartaric acid and its isomers).

765. Citric acid does not act very readily as a **reducing agent**; does not reduce alkaline copper solution, or silver solution, or permanganate but very slowly. Concentrated nitric acid produces from it, acetic and oxalic acids; and digestion with manganese dioxide decomposes it, with formation of acetone, acrylic, and acetic acids. Citrates carbonize on **ignition**, with various empyreumatic products, and with final formation of carbonates. By fused potassium hydrate, short of ignition, they are decomposed with production of oxalate and acetate.

PART III.

SYSTEMATIC EXAMINATIONS.

SEPARATION OF THE ACIDS FROM THE BASES.

766. The preliminary examination of **the Solid Material in the dry way** will give indications drawing attention to certain acids. Solutions can be evaporated to obtain a residue for this examination (12). Thus, *detonation* (not the decrepitation caused by water in crystals) indicates **chlorates, nitrates**, bromates, iodates. *Explosion* or *deflagration* will occur if these, or other oxygen-furnishing salts—as permanganates, chromates—are in mixture with easily combustible matter (518). Hypophosphites, heated alone, deflagrate intensely (725). A *brownish-yellow vapor* indicates **nitrates** or nitrites (602); a *green flame*, **borates** (730).—The *odor of burning sulphur:* **sulphides**, sulphites, thiosulphates, or free sulphur. The separation of *carbon black:* an organic acid (645). The formation of a *silver stain:* a *sulphur* **compound** (680).

767. When **dissolving a solid** by acids for work in the wet way, indications of the more volatile acids will be obtained. Sudden *effervescence:* a **carbonate** (oxalate or cyanate) (648, 649). *Greenish-yellow vapors:* a **chlorate** (520). *Brownish-yellow*, chlor-nitrous vapors on addition of hydrochloric acid: a **nitrate**.—The *characteristic odors:* salts of hydrosulphuric acid, sulphurous acid, hydrobromic acid, hydriodic acid, hydrocyanic acid, acetic acid.—The separation of *sulphur:* a higher **sulphide**, etc. It will be remembered that chlorine results from action of manganese dioxide, and numerous oxidizing agents, upon hydrochloric acid.

768. If the Material is in Solution, the bases will be first determined. (Certain volatile acids will be detected in the first group acidulation—by indications mentioned in the preceding paragraph.) Now, it should first be considered, what acids *can be present in solution with the bases found?* Thus, if *barium* be among the bases, we need not look for sulphuric acid nor, in a solution not acid, for phosphoric acid.

769. As a general rule, the non-alkali metals must be removed from a

solution before testing it for acids, unless it can be clearly seen that they will not interfere with the tests to be made.

Metals need to be removed: because, firstly, *in the testing for acids by precipitation*, a precipitate may be obtained from the action of the reagent on the base of the solution tested, thus: if the solution contain silver, we cannot test it for sulphuric acid by use of barium chloride (and we are restricted to use of barium nitrate). And, secondly, *in testing for acids by transposition with a stronger acid*—the preliminary examination for acids—certain bases do not permit transposition. Thus, chlorides, etc., of lead, silver, mercury, tin, and antimony, and sulphide of arsenic, are not transposed by sulphuric acid, or not promptly.

770. *If neither arsenic nor antimony* is among the bases, they may all be removed (*a*) by *boiling with slight excess of* sodium or potassium carbonate, and filtering. *Arsenic and antimony*, and all other bases of the second group, may be removed (*b*) by boiling with **hydrosulphuric acid**, and filtering. When the bases are removed by sodium or potassium carbonate, the filtrate *must be exactly neutralized* by nitric acid, with the *expulsion of all carbonic acid* by boiling. Then, for nitric acid, the original substance may be tested.

The filtrate, from the third or fourth group, though free from all bases which need to be removed, is not suitable material for general tests for acids; because it is loaded with ammonium salts, which act as solvents on many of the precipitates to be obtained.

771. The separation of **Phosphoric** acid from bases is a part of the work of the third group of metals, and is explained in 246 and 247. The removal of **Boracic** acid, **Oxalic** acid, **Silicic** acid, is described in 249.

The **non-volatile Cyanogen acids** can be separated from bases by digesting with potassium or sodium hydrate (not too strong, 624), adding potassium or sodium carbonate and digesting, and then filtering. The residue is examined for bases, by the usual systematic process. The solution (617 *c*) will contain the alkali salts of the cyanogen acids, and may contain metals whose hydrates or carbonates are soluble in fixed alkali hydrates.

CONVERSION OF SOLIDS INTO LIQUIDS.

772. Before the fluid reagents can be applied, solids must be reduced to liquids. To obtain a complete solution, the following steps must be observed:

First. The solid, reduced to a fine powder, is boiled in ten times its quantity of **water.** Should a residue remain, it is allowed to subside, and the clear liquid poured off or separated by filtration. A *drop* or *two* evaporated on glass, or clean and bright platinum foil, will give a residue, if any portion has dissolved. If a solution is obtained, the residue, if any, is exhausted, and well washed with hot water.

Second. The residue, insoluble in water, is digested some time with **hot hydrochloric acid.** (Observe 767.) The solid, if any remain, is separated by filtration, and washed, first with a little of this acid, then with water. The solution, with the washings, is reserved.

Third. The well-washed residue is next digested with hot **nitric acid.** Observe if there are vapors of nitrogen oxides, indicating that a metal or other body is being oxidized (590). Observe if sulphur separates, (464). If any residue remains, it is separated by filtration and washing, first with a little acid, then with water, and the solution reserved.

Fourth. Should a residue remain, it is to be digested with **nitro-hydrochloric acid,** as directed for the other solvents.

The acid solutions are to be evaporated nearly to dryness, and then redissolved in water, acidulating, if necessary, to keep the substance in solution.

Fifth. Should the substance under examination prove insoluble in acids, it is likely to be either a sulphate (of barium, strontium, or lead); a chloride, or bromide, of silver or lead; a silicate or fluoride—perhaps decomposed by sulphuric acid—(737); and it *must be fused with a fixed alkali carbonate,* when the constituents are transposed in such manner as to render them soluble. The watery solution of the fused mass will be found to contain the acid; the residue, insoluble in water, the metal, now soluble in hydrochloric or nitric acids (compare 677).

If more than one solution is obtained, by the several trials with solvents, the material contains more than one compound, and the solutions, as separated by filtration, should be preserved separately, as above directed, and analyzed separately. *The separate results, in many cases, indicate the original combination of each metal.*

CONVERSION OF SOLUTIONS INTO SOLIDS: Before solids in solution can be subjected to preliminary examination—either for metals or for acids—they must be obtained in the solid state. This is done by evaporation (see 12).

REMOVAL OF ORGANIC SUBSTANCES.

773. The methods of inorganic analysis do not provide against interference by organic compounds; and, in general, it is impossible to conduct inorganic analysis in material containing organic bodies. The removal of the latter can be effected, 1st, by combustion at a red or white heat, with or without oxidizing reagents; 2d (in part), by oxidation with potassium chlorate and hydrochloric acid on the water-bath; 3d, by oxidation with nitric acid in presence of sulphuric acid, at a final temperature of the boiling point of the latter; 4th, by solvents of certain classes of organic substances; 5th, by Dialysis. These operations are conducted as follows:

774. *Combustion at a red or white heat,* of course, excludes analysis for mercury, arsenious and antimonious bodies (except as provided in 425) and ammonium. The last-named constituent can be identified from a portion of the material in presence of the

organic matter (63 and 585). If chlorides are present, iron will be lost at temperatures much above 100° C., and potassium and sodium waste notably at a white heat, and slightly at a full red heat. Certain acids will be expelled, and oxidizing agents reduced.

The material is thoroughly dried and then heated, in a porcelain or platinum crucible, at first gently. It will blacken, by separation of the carbon of the organic compounds. The ignition is continued until the black color of the carbon has disappeared. In special cases of analysis, it is only necessary to char the material: then pulverize it, digest with the suitable solvents and filter; but this method does not give assurance of full separation of all substances. Complete combustion, without use of oxidizing agents, is the way most secure against loss, and entailing least change of the material: it is, however, sometimes very slow. The operation may be hastened, with oxidation of all materials, by *addition of nitric acid, or of ammonium nitrate.* The material is first fully charred: then allowed to cool till the finger can be held on the crucible; enough nitric acid to moisten the mass is dropped from a glass rod upon it, the lid put on, and the heat of the water-bath continued until the mass is dry, when it may be very gradually raised to full heat. This addition may be repeated as necessary. The ammonium nitrate may be added, as a solid, in the same way.

775. *Oxidation with potassium chlorate and hydrochloric acid on the water-bath* does not wholly remove organic matter, but so far disintegrates and changes it that the filtrate will give the group precipitates, pure enough for most tests. It does not vaporize any bases but ammonium, but of course oxidizes or chlorinates all constituents. It is especially applicable to viscid liquids; it may be followed by evaporation to dryness and ignition, according to 774.

The material with about an equal portion of hydrochloric acid is warmed on the water-bath, and a minute portion of potassium chlorate is added at short intervals, stirring with a glass rod. This is until the mixture is wholly decolored and dissolved. It is then evaporated to remove chlorine, diluted and filtered. If potassium and chlorine are to be tested for, another portion may be treated with nitric acid, on the water-bath. The organic matter left from the action of the chlorine or the nitric acid may be sufficient to prevent the precipitation of aluminium and chromium in the third group of bases; so that a portion must be ignited. As to arsenic and antimony, see 425.

776. The action of *sulphuric with nitric acid at a gradually increasing heat*, leaves behind all the metals (not ammonium), with some loss of mercury and arsenic (and iron?) if chlorides are present in considerable quantity. In this, as in the operations before-mentioned, volatile acids are lost—sulphides partly oxidized to sulphates, etc.

The substance is placed in a tubulated retort, with about four parts of concentrated sulphuric acid, and gently heated until dissolved or mixed. A funnel is now placed in the tubule, and nitric acid added in small portions gradually raising the heat, for about half an hour—so as to expel the chlorine, and not vaporize chlorides. The material is now transferred to a platinum dish, and heated until the *sulphuric acid begins to vaporize.* Then add small portions of nitric acid, at intervals, until the liquid ceases to darken by digestion, after a portion of nitric acid is expelled. Finally, evaporate off the sulphuric acid, using the lowest possible heat at the close.

777. *The solvents used* are chiefly *ether for fatty matter*, and alcohol or ether or both successively, for resins. Instead of either of these, benzene may be used; and many fats and some resins may be dissolved in petroleum naphtha. It will be observed, that ether dissolves some metallic chlorides, and that alcohol dissolves various metallic salts. Before the use of either of these solvents upon solid material, it should be thoroughly dried and pulverized. Fatty matter suspended in water solutions, may be approximately removed by filtering through wet, close filters; also, by shaking with ether or benzene, and decanting the solvent after its separation.

778. *By Dialysis*, the larger part of any ordinary inorganic substance can be extracted in approximate purity from the greater number of organic substances in water solution. The degree of purity of the separated substance depends upon the kind of organic material. Thus, albuminoid compounds are almost fully rejected; but saccharine compounds pass through the membrane quite as freely as some metallic salts. (Consult Watts' Dictionary, II., 316; III., 715.)

PRELIMINARY EXAMINATION OF SOLIDS.

779. Before proceeding to the analysis of a substance in the wet way, a careful study should usually be made of the reactions which the substance undergoes in the solid state, when subjected to a high heat, either alone or in the presence of certain reagents, before the blow-pipe, or in the flame of the Bunsen Burner. This examination in the dry way precedes that in the wet, and should be carried on systematically, following the plan laid down in the Tables, and noting carefully every change which the substance under investigation undergoes, and if necessary making reference to some of the standard works on Blow-pipe Analysis. In order to understand fully the nature of these reactions, the student should first acquaint himself with the character of the different parts of the flame, and the use of the blow-pipe in producing the reducing and oxidizing flame.

780. *The flame of the candle, or of the gas-jet*, burning under ordinary circumstances, consists of three distinct parts: a dark nucleus or zone in the centre, surrounding the wick, consisting of unburnt gas—a luminous cone surrounding this nucleus, consisting of the gases in a state of incomplete combustion. Exterior to this is a thin, non-luminous envelope, where, with a full supply of oxygen, complete combustion is taking place: here, we find the hottest part of the flame. The non-luminous or outer part is called the **oxidizing flame**; the luminous part, consisting of carbon and unconsumed hydrocarbons, is called the **reducing flame.**

781. *The flame produced by the Blow-pipe* is divided into two parts—the oxidizing flame, where there is an excess of oxygen corresponding to the outer zone of the candle-flame, and the reducing flame, where there is an excess of carbon, corresponding to the inner zone of the candle-flame. Upon the student's skill in producing these flames, depends very largely the results in the use of the blow-pipe.

In order to produce a good **oxidizing flame**, the jet of the blow-pipe is placed just within the flame, and a moderate blast applied—the air being thoroughly mixed with the gas, the inner blue flame, corresponding to the exterior part of the candle-flame, is produced: the hottest and most effective part is just before the apex of the blue cone, where combustion is most complete.

The **reducing flame** is produced by placing the blow-pipe just at the edge of the flame, a little above the slit, and directing the blast of air a little higher than for the oxidizing flame. The flame assumes the shape of a non-luminous cone, surrounded by a pale-blue mantle; the most active part of the flame is somewhat beyond the apex of the luminous cone.

782. The blast with the blow-pipe is not produced by the lungs, but by the action of the muscles of the cheek alone. In order to obtain a better knowledge of the management of the flame, and to practise in producing a good reducing flame, it is well to fuse a small grain of metallic tin upon charcoal, and raising to a high heat endeavor to prevent its oxidation, and keep its surface bright; or better, perhaps, to dissolve a speck of manganese dioxide in the borax bead on platinum wire—the bead becoming amethyst-red in the outer flame and colorless in the reducing flame. The beginner should work only with substances of a known composition, and not attempt the analysis of unknown complex substances, until he has made himself perfectly familiar with the reactions of at least the more frequently occurring elements.

The amount of substance taken for analysis should not be too large; a quantity of about the bulk of a mustard-seed being, in most cases, quite sufficient.

The physical properties of the substance under examination are to be first noted—such as color, structure, odor, lustre, density, etc.

Heating in Glass Tube Closed at One End.

783. The substance, in fragments or in the form of a powder, is introduced into a small glass tube, sealed at one end, or into a small matrass, and heat applied gently, gradually raising it to redness, if necessary with the aid of the blow-pipe. When the substance is in the form of a powder it is more easily introduced into the tube by placing the powder in a narrow strip of paper, folded lengthwise in the shape of a trough; the paper is now inserted into the tube held horizontally, the whole brought to a vertical position, and the paper withdrawn; in this way the powder is all deposited at the bottom of the tube. By this treatment in the glass tube, we are first to notice whether the substance undergoes a change, and whether this change occurs with or without decomposition. The sublimates, which may be formed in the upper part of the tube, are especially to be noted. Escaping gases or vapors should be tested as to their alkalinity or acidity, by small strips of red and blue litmus inserted in the neck of the tube.

Heat in Glass Tube Open at Both Ends.

784. The substance is inserted into a glass tube from two to three inches long, about one inch from the end—at which point a bend is sometimes made; heat is applied gently at first, the force of the air-current passing through the

tube being regulated by inclining the tube at different angles. Many substances undergoing no change in the closed tube, absorb oxygen, and yield volatile acids or metallic oxides. As in the previous case, the nature of the sublimate and the odor of the escaping gas are particularly to be noted. The reaction of sulphur, arsenic, antimony, and selenium, are very characteristic; these metals, if present, are generally easily detected in this way.

Heat in the Blow-pipe Flame on Charcoal.

785. For this test, a well-burned piece of charcoal is selected, and a small cavity made in that side of the coal showing the annual rings; a small fragment of the substance is placed in the cavity, and, if the substance be a powder, it may be moistened with a drop of water. The coal is held horizontally, and the flame made to play upon the assay at an angle of about twenty-five degrees. The substance is brought to a moderate heat, and finally to intense ignition. Any escaping gases are to be tested for their odor; the change of color which the substance undergoes, and the nature and color of the coating which may form near the assay, are also to be carefully noted. Some substances, as lead, may be detected at once by the nature of the coating.

Ignition of the Substance previously Moistened with a Drop of Cobalt Nitrate.

786. This test may be effected either by heating on charcoal, in the loop of platinum wire, or in the platinum-pointed forceps. A portion of the substance is moistened with a drop of the reagent, and exposed to the action of the outer flame. When the substance is in fragments, and porous enough to absorb the cobalt solution, it may be held in the platinum-pointed forceps, and ignited. The color is to be noted after fusion. This test is rather limited; Aluminium, Zinc, and Magnesium, giving the most characteristic reactions.

Fusion with Sodium Carbonate on Charcoal.

787. The powdered substance to be tested is mixed with the Soda in the palm of the hand, moistened and placed in the cavity of the coal. Some substances form, with soda at a high heat, fusible compounds—others infusible. Many bodies, as silicates, require fusion with alkali carbonate before they can be tested in the wet way. Many metallic oxides are reduced to metal, forming globules, which may be easily detected.

When this test is applied for the detection of sulphates and sulphides, the flame of the alcohol-lamp is to be substituted for that of the gas-flame, as the latter generally contains sulphur compounds.

Examination of the Color which may be imparted to the Outer Flame.

788. In this way, many substances may be definitely detected. The test may be applied either on charcoal or on the loop of platinum wire—preferably

in the latter way. When the substance will admit, a small fragment is placed in the loop of the platinum wire, or held in the platinum-pointed forceps, and the point of the blue flame directed upon it. If the substance is a powder, it may be made into a paste with a drop of water, and placed in the cavity of the charcoal, the flame being directed horizontally across the coal. The color which the substance imparts to the outer flame in either case is noted. In most cases the flame of the Bunsen Burner alone will suffice; the substance being heated in the loop of platinum wire—which, in all cases, should be first dipped in hydrochloric acid, and ignited, in order to secure against the presence of foreign substances. Those salts which are more volatile at the temperature of the flame, as a rule give the most intense coloration. When two or more substances are found together, it is sometimes the case that one of them masks the color of all the others—the bright yellow flame of Sodium, when present in excess, generally veiling the flame of the other elements. In order to obviate this, Bunsen has furnished us a method,* by the use of colored media (stained glasses, indigo solution, etc.) The appearance of the flame of various bodies, when viewed through these media, enables us often to detect very small quantities of them in the presence of large quantities of other substances.

Treatment of the Substance with Borax, and Microcosmic Salt.

789. This is best effected in the loop of platinum wire. This is heated and dipped into the borax or salt of phosphorus, and heated to a colorless bead; a small quantity of the substance under examination is now brought in contact with the hot bead, and heated, in both the oxidizing and reducing flames. Any reaction which takes place during the heating must be noticed; most of the metallic oxides are dissolved in the bead, and form a colored glass, the color of which is to be observed, both while hot and cold. The color of the bead varies in intensity, according to the amount of the substance used; a very small quantity will, in most cases, suffice. Certain bodies, as the alkaline earths, dissolve in borax, forming beads which, up to a certain degree of saturation, are clear. When these beads are brought into the reducing flame, and an intermittent blast used, they become opaque. This operation is called **flaming.**

As reducing agents, certain metals are employed in the bead of borax or salt of phosphorus. For this purpose, **Tin** is generally chosen—Lead and Silver being taken, in some cases. These metals cannot be used in the loop of platinum wire, as they will alloy the platinum. The beads are first formed in the loop of wire; then, while hot, shaken off into a porcelain dish, several being so obtained. A number of these are now taken on charcoal, and fused into a

* For a full account of the method of analysis by flame reactions and colored media, suggested by Cartmell; and by films on porcelain, as developed by Bunsen; consult *Watts' Dict.*, 1st Supplement, p. 125; also *Plattner's Manual, Blow-pipe Anal.*, Richter, N. Y.

large bead, which is charged with the substance to be tested, and then with the tin, or other metal. For this purpose tin foil (or lead foil) is previously cut in strips half an inch wide, and the strips rolled into rods. The end of the rod is touched to the hot bead, to obtain as much of the metal as required. Lead may be added as precipitated lead ("proof-lead"), and silver as precipitated silver. By aid of tin in the bead, cuprous oxide, ferrous oxide, and metallic antimony are obtained, and other reductions effected, as directed in 791 and elsewhere.

790. PRELIMINARY EXAMINATION OF SOLIDS.

Note physical properties, such as Structure, Gravity, Color, Odor, etc.

I. Heat a portion, finely pulverized, in a Dry Glass Tube, closed at one end (783).

1. *The Substance suffers no change:*

   Absence of volatile bodies (including combined water), of organic compounds, and of those which change color on heating.

2. *The Substance changes color:*

   Organic compounds *blacken* from separation of carbon, which burns away.
   Cu and **Co** salts *blacken* at high heat.
   ZnO and most **Zn** salts, *yellow while hot, white when cold.*
   PbO and **Pb** salts, *yellow while hot, yellow when cold.*
   Bi_2O_3 (white) and many **Bi** salts, *orange to red-brown while hot, pale-yellow when cold.*
   Fe_2O_3, and salts, *red to black while hot, reddish-brown when cold.*
   $Cd(OH)_2$ and many **Cd** salts, *brown while hot, brown when cold.*
   SnO_2, *brown while hot, yellow when cold.*

3. *The substance fuses:*

   Most **alkali salts** and numerous other salts. Many salts dissolve in their water of crystallization when heated, becoming solid again by vaporization.

4. *The substance sublimes*, partially or wholly:

   H_2O of crystallization, combination, or absorption.

   Sublimate condensing in cold part of the tube.

Hg (363) *gray*, easily rubbed to globules.
$HgCl_2$ first melts, then forms *white* crystalline sublimate.
Hg_2Cl_2, without melting, forms a sublimate, *yellow while hot, white when cold.*
HgS, a *black* sublimate, turning red on trituration.
As, *steel-gray* sublimate ; *garlic odor.*
As_2O_3, sublimes in *white* octahedral crystals, does not fuse (382).
As_2S_3, sublimate nearly *black while hot, reddish-yellow when cold.*
Sb_2S_3, fuses yellow ; forms *white*, amorphous sublimates.
NH_4 salts, those not decomposing, *white* sublimate (64).
Fe_2Cl_6, slowly sublimes as a reddish-yellow stain (192).
S, free or by reduction of sulphide, gives reddish-brown drops, yellow when solidified.
H_2CrO_4, a heavy white vapor and *crystalline* sublimate.
I, a violet vapor and *blue-black* sublimate.

5. *The substance evolves a gas or vapor :*

O, indicates the presence of a **nitrate, chlorate, bromate, iodate,** or **peroxide.** A small piece of coal placed upon the assay glows upon being heated.
H_2S, from hydrated **sulphides,** some **sulphites,** blackens *lead-paper.* Recognized by its odor.
SO_2, from **sulphites, thiosulphites,** certain **sulphates,** etc. Recognized by its odor and bleaching effect.
NH_3, from its compounds which decompose (64), *odor,* and alkaline *reaction on litmus.*
Cy, recognized by characteristic *odor* and violet *flame.*
Oxides of Nitrogen, from **nitrates or nitrites,** *reddish-brown, acrid vapor.*
Acetone, from **acetates**, characteristic fragrant odor.

II. Heat in a Glass Tube, open at both ends (784).

Certain of the changes stated above as occurring in operation I. are modified by oxidation. Oxides are obtained from metals.

S and Sulphides yield SO_2. Recognized by its odor and action on litmus-paper.

As yields a sublimate of As_2O_3.

Sb, yields a sublimate (white), of Sb_2O_3 and Sb_2O_5.

Bi, a sublimate, dark-brown while hot, lemon-yellow when cold (Bi_2O_3).

Te, gray sublimate of **tellurous acid** (TeO_2).

Se and **Selenides,** evolve SeO_2, odor resembling that of rotten horse-radish (499).

Hg, sublimate of metallic mercury.

III. Heat in the Blow-pipe Flame on Charcoal (785).

1. *The substance decrepitates:*

   Crystals containing water, as **NaCl.** (If finely pulverized, the decrepitation is avoided.)

2. *The substance deflagrates:*

   Nitrates, Chlorates, Iodates, Hypophosphites, Permanganates, etc.

3. *The substance fuses, and is absorbed by the charcoal:*

   Salts of alkalies and some salts of alkaline earths.

4. *The substance is infusible and phosphorescent:*

   Ba, Sr, Ca, Mg—the residue is alkaline to test-paper.

   Al_2O_3, **MgO, ZnO** (yellow while hot), not alkaline to test-paper.

5. *The substance forms an incrustation on charcoal:*

   Pb, *lemon-yellow while hot,* sulphur-yellow when cold. In thin layers, bluish-white, volatile with bluish flame.

   Bi, dark *orange-yellow while hot,* lemon-yellow when cold.

   Zn, *yellow while hot,* white when cold, greenish-white flame.

TABLE I.—*Continued.*

	Cd, *red-brown*, volatile, dark-yellow flame. **As**, *white.* Readily volatilized, distant from the assay, faint blue flame. **Sb**, *white*, pale-green flame. **Sn**, *faint-yellow while hot*, white when cold.
IV. The Substance (or incrustation of Test III., 5) **is moistened with solution Cobalt Nitrate and strongly ignited** (786).	1. *The mass or incrustation is colored:* **ZnO**—*yellowish-green.* **SnO**—*bluish-green.* **Sb_2O_5**—*dirty dark-green.* **Al_2O_3, SiO_2, phosphates**—*blue.* **MgO**—*flesh-color or pink.* **BaO**—*brick-red.* **SrO, CaO**—*gray.*
V. Heat with Na_2CO_3, on charcoal in the inner Blow-pipe Flame (787).	1. *Metallic grains are obtained:* **Bi, Sb**—*brittle.* **Pb, Cu, Sn, Au**—*malleable.* 2. *An infusible magnetic powder is obtained:* **Fe, Ni, Co.**
VI. Heated in the Blow-pipe Flame, or in the Bunsen Flame on Charcoal, or in a loop of platinum wire (788).	1. *The substance colors the outer flame:* (If Test V. does not reduce metal, heat *on platinum wire* for flame color, before the blow-pipe or in Bunsen's flame.) *Yellow:* **Na** and its salts, even in small quantities, impart an intense reddish-yellow. Other salts, even in large quantities, do not interfere with this reaction; viewed

through a green glass, appears orange yellow; moistened with sulphuric acid, the test is more delicate (50).

Violet: **K** and most of its salts, except borates, phosphates, and silicates, give bluish-violet flame, distinguished in presence of very small quantities of sodium compounds. Excess of the latter prevents the reaction; **Li** also masks the reaction. In presence of sodium, the potassium flame appears reddish-violet when viewed through a blue glass (44).

Red: **Ca** and its compounds produce a yellowish-red flame (110).

Sr and many of its salts yield a crimson flame, masked by much **Ba** (100).

Li and its salts produce a carmine-red flame (70). Sodium interferes with the reaction; Potassium does not.

Green: Yellowish-green—**Ba** and most of its salts. Also **Mo** and its compounds.

Emerald-green—**Cu** and most of its compounds (283).

Bluish-green—B_2O_3 and **phosphates.**

Yellowish-green—B_2O_3, best obtained by the addition of sulphuric acid. Heat on platinum wire until the sulphuric acid is expelled, then moisten with glycerine and ignite (733).

Whitish-green—**Zn.**

Blue: Light blue—**As** and many arsenic compounds.

Azure-blue—**Pb, Se.** Also, $CuCl_2$.

Greenish-blue—**Sb,** $CuBr_2$.

791. SCHEME OF BLOW-PIPE ANALYSIS.

ARRANGED BY PROF. T. EGLESTON.*

The substance may contain—**As, Sb, S, Se, Fe, Mn, Cu, Co, Ni, Pb, Bi, Ag, Au, Hg, Zn, Cd, Sn, Cl, Br, I,** CO_2, SiO_2, N_2O_5, H_2O.

1. Treat on Ch.† in the O.F. to find volatile substances; such as **As, Sb, S, Se, Pb, Bi, Cd**, etc.

a. If there are volatile substances present, form a coating and test it with S.Ph. and tin on Ch. for **Sb** (789), or to distinguish between **Pb** and **Bi** (298).

b. If there are no volatile substances present, divide a part of the substance into three portions, and proceed as in A.

α. Yellow coat, yielding with S.Ph. a black bead; disappearing with blue flame; no part of it yielding greenish **Sb** flame: **Pb** and **Bi.**

β. Yellow coat, generally with white border, yielding black or gray bead with S.Ph., disappearing with blue flame; also the border, disappearing with greenish flame: **Pb** and **Sb.**

γ. Yellow coat, very similar to *β*, but yielding no blue flame: **Bi** and **Sb.**

2. If **As, Sb, S, Se,** are present, roast a large quantity thoroughly on Ch., until no odor of arsenic, or sulphurous acid, is given off. Divide the substance into three portions, and proceed as in A.

A. **Treatment of the First Portion.**—Dissolve a very small quantity in borax on platinum wire in the O.F., and observe the color produced. Various colors will be formed by the combination of the oxides. Saturate the bead, and shake it off into the porcelain dish. Repeat this once or twice.

a. Treat these beads on Ch. with a small piece of lead, silver, or gold, in a strong R.F.

b. **Fe, Mn, Co,** etc., remain in the bead. If the bead spreads out on the Ch., it must be collected to a globule by continued blowing. Make a borax bead on platinum wire, and dissolve in it *some* of the fragments of the bead, reserving the rest for accidents.

* *Amer. Chem.*, II., 383.

† Ch., charcoal; O.F., oxidizing flame; R.F., reducing flame; S.Ph., salt of phosphorus or microcosmic salt.

c. **Ni, Cu, Ag, Au, Sn, Pb, Bi** are reduced and collected by the lead button (**Sn, Pb, Bi**, if present, partly volatilize). Remove the lead button from the bead while hot, or by breaking the latter when cold, on the anvil between paper, carefully preserving all the fragments.

d. If **Co** is present, the bead will be blue. If a large amount of **Fe** is present, add a little borax to prove the presence or absence of **Co**. If **Mn** is present, the bead, when treated on platinum wire in the O.F., will become dark violet or black.

e. If only **Fe** and **Mn** with no **Co** are present, the bead will be almost colorless. Look, here, for **Cr, Ti, Mo, U, W, V, Ta,** by the wet way.

f. Treat the button *c* on Ch., in the O.F., until all the lead, etc., is driven off; **Ni, Cu, Ag, Au,** remaining behind; or separate the lead with boracic acid.

g. Treat the residue *g* on Ch. in O.F. with S.Ph. bead, removing the button while the bead is hot.

h. If **Ni** and **Cu** are present, the bead will be green when cold. If **Ni** only, yellow; if **Cu** only, blue. Prove **Cu** by treating with tin on Ch. in the R.F.

i. For **Ag** and **Au** make the special test.

B. **Treatment of the Second Portion.**—Drive off all the volatile substances in the O.F. on Ch. Treat with the R.F., or mix with soda and then treat with the R.F. for **Zn, Cd, Sn.** If a white coating is formed, test with cobalt solution (786).

C. **Treatment of the Third Portion.**—Dissolve some of the substance in S.Ph. on platinum wire in O.F., observing whether SiO_2 is present or not, and test for **Mn** with potassium nitrate.

3. Test for **As** with soda on Ch. in the R.F., or with **dry** soda in closed tube (382).

4. Dissolve in soda on platinum wire in the O.F. (if the substance is not metallic and does not contain any **S**) and test for **Sb** on Ch. with tin in the R.F. (789).

5. Test for **Se** on Ch. (499).

6. In absence of **Se**, fuse with soda in the R.F., and test for **S** on silver foil (669). In presence of **Se** test for **S** in open tube (662) to distinguish between **S** and SO_2.

7. Test for **Hg** with **dry** soda in a closed tube (363).

8. Mix some of the substance with assay lead and borax-glass and fuse on Ch. in the R.F. Cupel the lead button for **Ag**. Test with nitric acid for **Au** (477).

9. Test for **Cl**, **Br**, and **I**, with a bead of S.Ph., saturated with oxide of copper (516). With **Br**, the flame is blue with green tint; with **I**, the flame is green.

10. Test for **Cl**, or **Br**, with acid sulphate of potassium.

11. Test for H_2O, in a closed tube.

12. Test on platinum wire, or in platinum pointed forceps, for coloration in the flame (790, VI.)

13. Test for CO_2 with **HCl**.

14. Test for N_2O_5 with acid sulphate of potassium

15. Test for **Te** in an open tube (499)

792. BEHAVIOR OF SUBSTANCES BEFORE THE BLOW-PIPE WITH MICROCOSMIC SALT AND BORAX.

A clear bead is formed by fusing the flux on a loop of platinum wire. Dip the bead in the finely powdered substance to be examined, and heat again—first, in the oxidizing flame; second, in the reducing or inner flame. Metallic salts are mostly changed to oxides.

In the Table—*h.* signifies hot; *c.*, cold; *sups.*, supersaturated with oxide; *s. s.*, strongly saturated; *h. c.*, hot and cold.

Color of the Bead.	With Microcosmic Salt or Phosphate of Ammonium-sodium.		With Borax or Diborate of Sodium.	
	In outer or oxidizing Flame.	*In inner or reducing Flame.*	*In outer or oxidizing Flame.*	*In inner or reducing Flame.*
Colorless.	Si (swims undissolved). Al, Mg, Ca, Sr, Ba, Sn, (*s. s., opaque*) Ti, Zn, Cd, Pb, Bi, Sb, (*not sat.*)	Si (swims undissolved). Al, Mg, Ca, Sr, Ba, (*sups. not clear*). Ce, Mn, Sn.	*h., c.:* Si, Al, Sn, (*sups. opaque*). Al, Mg, Sr, Ca, Ba, Ag, (*not sat.*) Zn, Cd, Pb, Bi, Sb, Ti, Mo.	Si. Al, Sn, (*s. s., opaque*). Alkaline earths and earths. *h. c.:* Mn, Ce. *h.:* Cu.
Yellow or Brownish.	*h.* (*s. s.*): Fe, Ur, Ce. *c.:* Ni.	*h.:* Fe, Ti. *c.:* Ni.	*h., not sat.:* Fe, Ur. *h., sups.:* Pb, Bi, Sb.	*h.:* Ti, Mo.
Red.	*h.* (*s. s.*): Fe, Ni, Cr, Ce.	*c.:* Cu. *h.:* Ni, Ti with Fe.	*h.:* Fe, Ce. *c.:* Ni.	*c.:* Cu (*sups. opaque*).
Violet or Amethyst.	*h., c.:* Mn.	*c.:* Ti.	*h., c.:* Mn. *h.:* Ni with Co.	*c.:* Ti.
Blue.	*h., c.:* Co. *c.:* Cu.	*h., c.:* Co. *c.:* W.	*h., c.:* Co. *c.:* Cu.	*h. c.:* Co.
Green.	*h.:* Cu, Mo; Fe with Co or Cu. *c.:* Cr.	*c.:* Cr. *h.:* Ur, Mo.	*c.:* Cr. *h.:* Cu, Fe with Co.	Cr. *sups.:* Fe.
Gray and Opaque.		Ag, Pb, Sb, Cd, Bi, Zn, Ni.		The same as with Microcosmic salt.

793. GROUPING OF THE METALS.

(Compare 28–30. Remove each group before testing for the next.)

I. *Add* **Hydrochloric Acid,** *a drop at a time, as long as a precipitate is produced; warm, agitate, and filter* (446).

Precipitate: GROUP I.

Lead, $PbCl_2$, *white.*

Silver, $AgCl$, *white.*

Mercurosum, Hg_2Cl_2, *white.*

Proceed by 794.

For Rare Metals, see 256, 493, 499.

Concerning ambiguous results, see 447.

II. *To the Filtrate, or, if Group I. is absent, to original solution + HCl, add* **Hydrosulphuric Acid** *in excess; warm and filter* (452).

Precipitate: GROUP II.

Arsenic, As_2S_3, *yellow.*

Antimony, Sb_2S_3 or Sb_2S_5 *orange.*

Tin, SnS, *brown.* SnS_2, *yellow.*

Lead, PbS, *black.*

Bismuth, Bi_2S_3, *black.*

Copper, CuS, *black.*

Cadmium, CdS, *yellow.*

Mercury, HgS, *black.* (First, white to yellow.)

Proceed by 795.

Rare Metals: 475 to 499.

III. If phosphates may be present (246), test, after expelling H_2S by boiling, for PO_4, by 714. **In absence of Phosphates,** *proceed by* 242 A *and* B (*or by* 242½ *or* 796). **In Presence of Phosphates,** *proceed by* 797 *or by* 248.

Precipitates: GROUP III.

In absence of Phosphates:

A. *By ammoni'm hydrate and chloride.*

- Aluminium, $Al_2(OH)_6$, *white, gelatinous.*
- Chromium, $Cr_2(OH)_6$, *bluish-green.*
- Ferricum, $Fe_2(OH)_6$, *reddish-brown.*

B. *By ammoni'm sulphide.*

- Manganese, **MnS**, *flesh-colored.*
- Cobalt, **CoS**, *black.*
- Nickel, **NiS**, *black.*
- Zinc, **ZnS** *white.*

The entire group, by Ammonium Sulphide, Chloride, and Hydrate, the same as above, except Iron, **FeS**, *black.*

In Presence of Phosphates:

By ammonium sulphide, etc.
All as above (iron as **FeS**) and **Ba, Sr, Ca, Mg, Al, Cr,** as Phosphates, *white.*

For Rare Metals, see 251 to 257.

IV. *To the Filtrate from Group III.*, containing **Ammonium Chloride**, *add* **Ammonium Carbonate** *and* **Hydrate**; *digest with gentle heat (not boiling) for some time, and filter.*

Precipitate: GROUP IV.

Barium, $BaCO_3$, *white.*

Strontium, $SrCO_3$, *white.*

Calcium, $CaCO_3$, *white.*

Proceed by 798.

V. *The Filtrate contains:*

GROUP V.

Magnesium salts.

Ammonium salts.
Potassium "
Sodium "
Lithium "

Proceed by 799.

For Rare Metals, see 72.

The Precipitate is washed on the filter with one or two small portions of cold water; then treated with much **hot water**, *and filtered.*

Solution : $PbCl_2$ (313).

Test for Lead (449) *by*

Sulphuric acid, giving $PbSO_4$, *white.*

Hydrosulphuric acid, **PbS**, *black.*

Chromate, ... **$PbCrO_4$**, *yellow.*

Iodides, ... **PbI_2** (315).

The precipitates may be tested by the blow-pipe (323).

For the study of lead, see the Table at 364 *and the text at* 309.

Remaining Precipitate : AgCl, Hg_2Cl_2.

Digest with dilute, warm **Ammonium Hydrate**, *and filter* (16).

Solution: $(NH_3)_3(AgCl)_2$.

Test for silver (450), *after expelling any excess of ammonia by boiling, by acidulating slightly with* **nitric acid.** A precipitate is **AgCl.**

For other tests, the silver chloride may be reduced to the metal by **zinc** (340), or on **charcoal** before the blow-pipe (341), and the metal dissolved by **nitric acid** (326), the resulting solution giving all the reactions of silver.

If the original solution does not contain non-alkali metals, it may be used to obtain the characteristics of silver.

Follow the Table at 364, *and refer to the text at* 330.

Residue : NH_2Hg_2Cl, *black* (347).

[Lead Oxychloride, *white*, 448.]

The black color is the evidence of mercury. Additional proof may be obtained by testing the residue, or a portion of it, for mercury by drying and heating with **sodium carbonate**, in a glass tube (363).

For reactions of mercury in solution, if the original solution contains non-alkali metals, dissolve the residue with **nitro-hydrochloric acid**—as mercuric chloride.

Follow 364, *and refer to the text at* 346. *Also see* 795 "B."

795. ANALYSIS OF GROUP II. (Explanation at 455.)

Wash the precipitate thoroughly on the filter, and then digest (in the test-tube, 16) with **yellow ammonium sulphide**,* *using as little as possible. Treat the* **Residue**, *well-washed, as directed in "B." Precipitate the* **Filtrate** *with dilute* **hydrochloric acid** *(diluting with solution of hydrosulphuric acid), and filter; examining this* **Precipitate**,† *when washed, for* **As, Sb, Sn**, *according to "A."* [For Gold, 477; Platinum, 482. Rare Metals, 498.]

"A." **Precipitate from the Ammonium Sulphide Solution: As_2S_3, Sb_2S_5, SnS_2, (S).**

Treat the washed precipitate with **hydrochloric acid**, *and, if it does not dissolve, add a minute fragment of* **potassium chlorate**, *and digest in a test-tube, till the sulphides are dissolved (or decolored). Filter out any sulphur, washing the filter with a few drops of hydrochloric acid, and receiving the filtrate in an evaporating dish. Remove all the chlorine by a very gentle heat, until wet litmus-paper is not bleached by the vapor. Transfer to the Generator of a* **Marsh's Apparatus** *(carefully rinsing in any white residue of antimony or tin oxides)* (458).

Solution :‡ H_3AsO_4, $H_4Sb_2O_7$, $SnCl_4$.

Place in the Generator sufficient **zinc** *(a piece of platinum foil or wire) and* **dilute sulphuric acid** (or use Na-amalgam, **Al**, or **Mg**, 373 and 434), *and receive the gas in solution of* **silver nitrate** *(as long as a precipitate is produced). Now filter, and wash the residue.*

In the Generator : Sn, (**Sb**, **Zn** salt).	**Precipitate**, from SbH_3: Ag_3Sb, (**Ag**).	**Solution**, from AsH_3 : H_3AsO_3 ($AgNO_3$, HNO_3).
Gather and wash the solid contents of the generator; dissolve with moderately dilute **hydrochloric acid**, *as directed in* 435. (An undissolved residue may be **Sb**, soluble in nitro-hydrochloric acid.) *Test the solution* ($SnCl_2$) *for tin by* $HgCl_2$: *a white or gray precipitate* (437).	*Digest with warm* **hydrochloric acid** *to dissolve the antimony* (411), *dilute (not to precipitation), and test the solution for antimony by—* H_2S: *an orange precipitate.* **Water** : *a white precipitate* (402). Spots and Mirror, from SbH_3 (376).	*Remove the silver by adding just enough* **hydrochloric acid** *and filtering.* *Test the solution for arsenic by—* H_2S: *a yellow precipitate.* $AgNO_3$: (377). Spots from the flame (376). Sublimation from the sulphide (381).
Follow 445, and the text, at 429 and after.	Follow 445, and consult the text, at 402.	Follow 445, and consult 367 and after.

* If Copper is present, and Mercury absent, it is better to use **sodium sulphide** (457).

† A white precipitate, of sulphur, will occur in any case. Colored precipitates indicate **As**, **Sb**, or **Sn** (456).

‡ In many cases, the original solution can be used for additional results through Marsh's Test (373).

795. "B." SULPHIDES NOT SOLUBLE IN AMMONIUM SULPHIDE: PbS, Bi_2S_3, CuS, CdS, HgS.*

If sulphides have been found in "A," the precipitate should be washed, first with $(NH_4)_2S_2$ (or Na_2S), *then with water. Dissolve the precipitate by action of hot, moderately dilute* **nitric acid** (464). *Evaporate the solution to expel excess of nitric acid.*

Residue:

HgS, S [$PbSO_4$].

Dissolve the (black) precipitate by **nitrohydrochloric acid,** *and expel free chlorine by boiling* (471).

Solution: $HgCl_2$.

Test for mercury by **Stannous chloride** (362 *a*).
Ammonia (357).
Copper (362 *d*).
Sublimation (333).

Follow 364 *and the Text at* 356 *and after.*

Solution: $Pb(NO_3)_2$, $Bi(NO_3)_3$, $Cu(NO_3)_2$, $Cd(NO_3)_2$.

To a portion of the solution, add a drop of very dilute **sulphuric acid.** *If a precipitate appears* (465), add the reagent to the whole solution, and filter.

Precipitate:

$PbSO_4$.

Add chromate, and heat (467).
(Lead chromate dissolves in potassium hydrate, and reprecipitates with acetic acid.)
Test the pre. of sulphates, or sulphide, by reduction on charcoal (323).

See 794. *Follow* 364, *and the Text at* 309.

Filtrate: Bi, Cu, Cd, salts.

Add **ammonium hydrate** *to a slight alkaline reaction.*

Precipitate:

$Bi(OH)_3$

Filter out, and wash the precipitate and test it by **stannite,** *according to* 297. *Or, test by dissolving with a very little* **HCl** *on a watch-glass and adding water* (288).

Follow 302, *and the text at* 287.

Blue Solution: Copper (274), **cadmium** (301).

Concentrate in an evaporating dish, acidify with acetic acid, and confirm with **ferrocyanide;** *a brown precipitate,* **Cu_2FeCy_6.** *Test this, or the original solution, with metallic iron* (280).

For copper, follow 302 *and* 273.

If copper is present, treat the sulphide obtained by adding **H_2S** *to the ammoniacal solution, by one of the methods given in* 470, *for separation of cadmium.*

Colorless Solution: Cadmium, absence of copper.

To the concentrated (acidified or alkaline) solution, add **H_2S:** *a yellow precipitate,* **CdS.**
Ferrocyanide: Cd_2FeCy_6, *white.*
Cyanides (301).

For Cadmium, see the text at 3 2.

* If silver was not removed in the first group, it may be tested for, in the nitric solution of this precipitate, by **HCl.**

796. ANALYSIS OF GROUP III., IN ABSENCE OF PHOSPHATES.

The Scheme of Separations given in 242, is preferred to this, in most Cases. Also, Alternative, 242½.

To the filtrate from the second group (793), *add* **NH_4OH** *till alkaline, then add* **NH_4Cl** *and* **Ammonium Sulphide.**

Dissolve the well-washed Precipitate, on the Filter, by dilute, **cold hydrochloric acid** (244). *Concentrate in an evaporating dish.*

Solution: $ZnCl_2$, Al_2Cl_6, $FeCl_2$ (186), **$MnCl_2$, Cr_2Cl_6, $NiCl_2$, Cr_2Cl_6, $CoCl_2$, $NiCl_2$.**

Residue: CoS, NiS, *black. Test black residue by the blow-pipe for cobalt and nickel. Dissolve by nitric acid, and test for* **Ni,** *by* 229. *Add* **potassium hydrate** *solution to strong supersaturation and boil a short time* (235). *Filter, and wash.* Separation of **Zn** and **Al.**

Solution: K_2ZnO_2; $K_2Al_2O_4$.

Divide the solution into two portions.

Precipitate : $Fe(OH)_2$ and **$Fe_2(OH)_6$, $Mn(OH)_2$, $Cr_2(OH)_6$, $Co(OH)_2$, $Ni(OH)_2$.**

Examine five portions ; two in solution (for **Fe** and **Ni**), *and three in precipitate* (for **Cr, Mn, Co**).

1. For Zinc.	2. For Aluminium.	1 and 2. For Iron and for Nickel.	3. For Manganese.	4. For Chromium.	5. For Cobalt.
Add **ammonium sulphide** ; a precipitate, **ZnS** (237).	*Add* **Ammonium chloride** *in decided excess* (235). *A precipitate :* **$Al_2(OH)_6$.**	*Dissolve with a drop or two of* **nitro-hydrochloric acid,** *and expel all free chlorine.*	*Boil with* **PbO_2** *and* **HNO_3,** *as directed in* 210; *a red color,* **$HMnO_4$.** *Or fuse with* **Na_2CO_3** *and* **KNO_3,** *as directed in* 211 ; *a green mass, manganate, as* **K_2MnO_4.**	(*If* **Mn** is present, proceed by 242, with the filtrate from 2d group). *Fuse with* **Na_2CO_3** *and* **KNO_3** (159 *d*), *dissolve in water, acidify by acetic acid and test for chromic acid, by* 163, 164, 165. *Test, also, the original solution for chromic acid* (155).	*Test in the* **borax** *bead* (224).
This precipitate may be dissolved by **HCl,** *or, in absence of interfering bases, the original solution taken, for additional tests for zinc.*	*Dissolve and test this solution, or test the original solution, if free from interfering bases, for aluminium.*	*Test a portion for Iron by* **potassium sulphocyanate** : a red solution, **$Fe_2(CyS)_6$.** *Test the original solution for Ferrosum and Ferricum by* ferricyanide *and* sulphocyanate, 193.			
		For Iron, follow the text at 174, *and after.*			
Follow 241, *and the text at* 235.	*Follow* 241, *and the text at* 145.	*Test a portion for* **Nickel,** *by* 229 *or* 230.	*Follow* 241, *and consult the text at* 204, *and after.*	*Follow* 241, *and the text at* 154 *and after.*	*Consult the text at* 219.

797. ANALYSIS OF GROUP III., IN PRESENCE OF PHOSPHATES. (Explanation in 246.)

[The Scheme at 248 may be used instead of this one.]

To the Filtrate from Group II., add **ammonium chloride**, *and* **ammonium hydrate** *to alkaline reaction, then* **ammonium sulphide** *to complete the precipitation.* Reserve the Filtrate for Group IV.

Precipitate : FeS, MnS, CoS, NiS, ZnS, S; $Al_2(OH)_6$, $Cr_2(OH)_6$; phosphates of Al, Cr, and of Ba, Sr, Ca, Mg.

***Treat** the well-washed precipitate with cold dilute* **hydrochloric acid.** *If a black residue remains, test it for* **Co** *and* **Ni**, *as directed in the Table at* 242 *b. Also, this residue may be tested for* **Si** (738). *The filtered solution is boiled to expel* H_2S, *filtered if turbid, and a smaller portion reserved.*

Portion 1.

Add a few drops of **nitric acid** *and boil.*

Solution : Fe_2Cl_6, Al_2Cl_6, Cr_2Cl_6, $MnCl_2$, [$CoCl_2$, $NiCl_2$], $ZnCl_2$, H_3PO_4, (H_2SiO_3); also **Ba, Sr, Ca, Mg, chlorides.**

(1). *Test a small portion for iron, by* **sulphocyanate.** If iron is found, *test the original solution by* **ferricyanide** *and* **sulphocyanate** *as directed in* 193.

(2). *To the remainder, add* **ferric chloride** *till a drop is precipitated yellow by ammonium hydrate* (showing that the PO_4 is all precipitated), *concentrate to a small bulk, add water, nearly neutralized by* K_2CO_3, *and add excess of* **barium carbonate.** *Let the mixture stand and filter.*

Portion 2.

Solution; $BaCl_2$, $SrCl_2$ $CaCl_2$, $MgCl_2$, etc.

Add **sulphuric acid** *and filter.*

Precipitate: $BaSO_4$, $SrSO_4$ ($CaSO_4$).

Test the **precipitate** *for* **Sr**, *by the flame.* [*Test it for* **Ba** *by boiling with* K_2CO_3 (677), *then dissolving the well washed precipitate by acetic acid and obtaining reactions with chromate, etc.*]

To the **filtrate**, *add* **alcohol.** A precipitate may be $CaSO_4$. *Boil with water and add* NH_4OH *and* **oxalate**, *for* **calcium.**

Precipitate ; $Al_2(OH)_6$, $Cr_2(OH)_6$, [$Fe_2(PO_4)_2$, $Fe_2(OH)_6$ $BaCO_3$].

Boil the precipitate for some time with sodium or **potassium hydrate.**

Solution; $K_2Al_2O_4$.

Acidify the solution with **HCl** *and add excess of* **ammonium hydrate** *and boil.*

Precipitate; $Al_2(OH)_6$.

Follow the text at 141.

Precipitate; $Cr_2(OH)_6$, etc.

Test for **chromium** as directed in 242 (p. 72).

Solution; $MnCl_2$, $ZnCl_2$, $BaCl_2$, $SrCl_2$, $CaCl_2$, $MgCl_2$.

Add **HCl** *and boil to expel* CO_2. *Add* NH_4OH *to alkaline reaction, then* **ammonium sulphide**, *and warm and filter.*

Precipitate: MnS, ZnS.

Dissolve by **HCl*** *and test the solution* ($MnCl_2ZnCl_2$) *by the directions in* 242 (B), p. 73. [*Or separate by* Acetic Acid, 236.]

* If a black residue appear, test for cobalt and nickel, as directed in foot-note 242 B.

Filtrate: $BaCl_2$, $MgCl_2$.

Remove **Ba, Sr, Ca**, *by adding* H_2SO_4, *as directed in* **Portion 2**, *above, then add* ammonium **oxalate** *and hydrate, filter, and test the* **filtrate** *for* **Mg**, *by adding* **phosphate.**

798. ANALYSIS OF GROUP IV. (Explanation in 121.)

[The Method of Separation given in 125 may be used instead of this.]

[Concerning the loss of traces of barium and calcium, see 123.]

Dissolve the well-washed precipitate in dilute **acetic acid.** **Solution: $Ba(C_2H_3O_2)_2$, $Sr(C_2H_3O_2)_2$, $Ca(C_2H_3O_2)_2$.**

To a small portion of the solution, add **potassium dichromate**; *if a precipitate appears, add the reagent to the whole solution as long as a precipitate is produced* (89), and filter.

Precipitate: $BaCrO_4$, *yellow.*	**Solution: $Sr(C_2H_3O_2)_2$, $Ca(C_2H_3O_2)_2$, $[K_2Cr_2O_7]$.**	
The precipitate is soluble by hydrochloric acid, and this solution is precipitated by **sulphuric acid,** *as* **$BaSO_4$,** *insoluble in acids.*	*Precipitate by* **ammonium carbonate** *with* **ammonium hydrate**; *filter, and wash the precipitate, and dissolve it by* **hydrochloric acid.** *Evaporate in a porcelain dish at a gentle heat, nearly or quite to dryness; then add a little water, to obtain a concentrated solution, nearly or quite neutral.* **Solution; $SrCl_2$, $CaCl_2$.** *Divide in two portions.*	
See 120, *and the text, at* 86 *and after.*	**For Strontium:** *To a portion, add solution of* **calcium sulphate**; *boil, and leave for about ten minutes. A precipitate indicates strontium,* **$SrSO_4$.** *Test another portion of the solution on a loop of platinum wire, by the flame* (790, VI.)	**For Calcium:** *Add solution of* **potassium sulphate** (*and filter*), *to insure the absence of strontium.* *To the filtrate* (*or solution not precipitated*), *add* **ammonium hydrate** *and* **ammonium oxalate.** A precipitate: **CaC_2O_4,** insoluble in acetic acid, soluble in hydrochloric. *Test by the flame* (790, VI.)
	See the text, at 98.	*Follow* 120 *and the text at* 104.

Evaporate a drop or two on clean platinum foil by a gentle heat (36). *If a residue is obtained, ignite. If the residue or a part of it vaporizes immediately,* **ammonium compounds** *are indicated.* (*The melting of fixed alkali salts is liable to be mistaken for vaporization.*)

For Ammonium, *test a portion of the original material with* **calcium,** *or* **potassium,** *or* **sodium hydrate,** *at a gentle heat. The vapor of ammonia,* NH_3, is recognized *by its effect on moistened* litmus-paper, *its odor, etc.* (57).

Test the solution by potassium mercuric iodide with potassium hydrate; by mercuric chloride, etc.

Consult 58 to 65.

For Magnesium, test the **Filtrate from Group IV.**

Add a little **ammonium hydrate**; *then enough* ammonium chloride *to dissolve any precipitate which appears* (117) *and then* **sodium phosphate.** Precipitate: $MgNH_4PO_4$.

Concerning lithium phosphate, see 68.

Calcium, in traces, may appear here, as phosphate (123). To guard against this fallacy, add oxalate to the filtrate from the fourth group, and filter out any precipitate so made.

Follow 120, *and the text at* 114 *and after.*

If magnesium is present, its compounds lessen the delicacy of the Flame Tests for the Metals of the Alkalies, and wholly prevent tests by precipitation.

To remove Magnesium, *precipitate it by* **barium hydrate** *and then remove the barium, as directed in* 130.

For Potassium, *test by the flame* (on platinum wire, with the Bunsen burner); *violet, not obscured by blue glass* (44).

Test by Tartaric acid, *using a concentrated solution.*

Follow the text at 40 *to* 45, and 788. (See 790, VI.)

For Sodium, *test* (*on platinum wire*) *for the flame color, yellow, and given by extraneous traces of sodium compounds* (52). *Obscured by the blue glass.*

Follow the text at 48 *and after, and* 790, VI.

For Lithium, *test by the flame, crimson, and obscured only by very thick blue glass* (70).

Test by **sodium phosphate.** The precipitate, Li_3PO_4, is soluble in much ammonium chloride (distinction from magnesium).

800. PRELIMINARY EXAMINATION FOR ACIDS.

Concerning the indications of acids in the Blow-pipe Examination, see 766 and 790; the indications in dissolving Solids, see 767; the considerations relative to any Bases already determined, see 768; the Removal of Bases, see 769–771; Reactions in the Wet Way, see 801.

For the Vaporous Acids :

I. To a little of the solid substance or residue by evaporation, or very concentrated solution, in a test-tube, add a little concentrated Sulphuric Acid, and heat gently, not enough to vaporize the sulphuric acid.

If the vapor reddens moist blue litmus-paper, some one or more of the following-named volatile acids is indicated:

1. *There is sudden effervescence:*

Carbonic anhydride, CO_2. *Colorless and odorless gas,* feebly reddening litmus, and making **solution of calcium hydrate** turbid. See 649. If the original substance contains non-alkali bases in solution, carbonates cannot be present. Solutions of carbonates give precipitates with salts of **all non-alkali metals**—651 and 30. Comparison of Effervescent Acids, 696.

Oxalates (653) and **cyanates** (635) also evolve **CO_2.**

2. *Effervescence of gas having odor:*

Hydrosulphuric acid, H_2S. *Blackens paper wet with lead acetate.* Most sulphides are transposed by **hydrochloric acid** with evolution of **H_2S**; by **nitric acid** or **chlorine** with separation of **S.** Sulphides in solution precipitate salts of **the first three groups of bases** (667). See Test II., and 703. **Reactions compared in** 696.

Sulphurous anhydride, SO_2. *Odor* of burning sulphur. Bleaches **litmus.** Colors iodic acid and starch (692). Sulphites precipitate salts **of all non-alkali bases.** Follow 696 and the text at 685.

Thiosulphates, also, evolve sulphurous anhydride, on decomposition—sulphur being separated, 697. Decomposed by all acids. Form precipitates (699), soluble in excess.

Hydrocyanic acid, HCy. Peach-blossom *odor*. Gas precipitates **silver nitrate**, on a glass rod, as **AgCy**. Change to *Sulphocyanate*, gives blood-red color with ferric salts (622); to ferrocyanide, gives blue color with iron salts (621). Alkali cyanides are decomposed by all acids. In solution, they precipitate most of the second and third group metals (619). **Reactions compared in** 696.

Acetic acid, $H(C_2H_3O_2)$. *Odor* of vinegar. Digested with alcohol and sulphuric acid, gives odor of *acetic ether* (754). Acetates are decomposed by hydrochloric and nitric acids. In solution, form **no precipitates,** but give red solution with ferric salts (753).

Hydrochloric acid, HCl. Slight effervescence. Slight, irritating *odor*. The gas forms a white precipitate (**AgCl**) with solution of **silver nitrate,** on a glass rod; the precipitate being insoluble in dilute nitric acid, but soluble in ammonium hydrate (509). The gas forms a white cloud with vapor of ammonia. Chlorides precipitate salts of all the **first group bases** (508). Compare the reactions by **table** at 574. For separations, see 576.*

3. *Appearance of gas having color:*

Hydriodic acid, HI. *Odor* is offensive, and slightly chlorine-like. Vapor *colors* violet in the air—both odor and color due to separation of free iodine. Vapor and mixture color **starch** blue. **Carbon disulphide** extracts iodine, violet. Soluble iodides decomposed by hydrochloric and nitric acids. In solution, give colored precipitates with salts of the **first group metals** (see 559 to 565). Compare reactions by **table**, 574. For separations, see 576.

Hydrobromic acid, HBr. *Odor* is acrid and chlorine-like. *Color*, slightly yellowish brown—odor and color due to separation of free bromine. **Starch** colors yellow;

* For a new application of the chlorochromic test, by Prof Wiley, see *Chem. News*, xli. 176, April 16, 1880.

Carbon disulphide yellow; iodine being absent in both tests. Soluble bromides transposed by hydrochloric and nitric acids. In solution, give yellowish-white or white precipitates with **salts of the first group bases** (536). Compare reactions, by aid of the **table** at 574. For separations, see 576.

Nitrous acid, HNO_2, and nitric peroxide, N_2O_4, characteristic acrid *odor*. *Color*, red-brown. Color potassium iodide and starch, blue. Salts all soluble. See the text at 605.

The brown gas is produced very sparingly from **nitrates** (unless reducing agents are present), but produced abundantly from **nitrites**. See special Tests (III.)

Chloric acid, $HClO_3$. *Detonation* with sulphuric acid. *Odor* of chlorine. *Color*, greenish-yellow. Gas bleaches litmus. Chlorates decomposed by hydrochloric acid (522) and by nitric acid. By **ignition**, reduced to chlorides. Form **no precipitates**, except by reduction (compare reactions by the **table** at 574).

Chlorine, Cl, is evolved in the decomposition of **hypochlorites** (524), and in that of chlorides with oxidizing agents (510).

II. Fuse with pure Sodium Carbonate, *on charcoal,* **and test the mass obtained.**

1. *When moistened, it blackens silver:*

Indications of **sulphur** in any combination or uncombined (669 and 703).

Fusion with sodium carbonate on platinum foil or in a porcelain capsule. The mass blackens silver: a **sulphide** or **thiosulphate**. The mass does not blacken silver: a **sulphate**. Concerning precipitates by these acids, see 703. Reactions of sulphuric acid compared, 720; hydrosulphuric, 696.

2. *When acidified with hydrochloric acid,* filtered, and the filtrate *evaporated to dryness* and treated with the same acid, *an insoluble residue is obtained:* **Silicic anhydride, SiO_2.** Soluble in boiling solutions of fixed alkalies. See 738 and the bead-test (792).

III. Certain Tests not classified.

1. *For Nitric acid and Nitrous acid:*

Trial to be made, in case of any material soluble in water (593 and 612). Only slight portions of nitrites could escape recognition by the brown gas evolved in Test I., as above mentioned. Nitrates, with reducing agents, evolve brown gas abundantly, in Test I.

Test for Nitric and nitrous acids, by formation of the "brown ring" (596).

Tests for Nitrous acid by 608 and 607.

2. *For Boric acid:*

Borates of non-alkali metals, insoluble (728). See Flame Test, 790, VI. Test by 730 and 733.

3. *For Silicic acid:*

Compounds insoluble, except those giving a very strong alkaline reaction. See test in the bead, 792. See Test II., 2, above.

4. *For Hydroferrocyanic, Hydroferricyanic, and Sulphocyanic acids:*

Heated with sulphuric acid, evolve **HCy** (627).

Sulphocyanates, fused with KNO_3, form soluble *sulphate.*

Insoluble salts of H_4FeCy_6, and H_3FeCy_6, boiled with solution of **KOH,** form soluble potassium salts (617 *c*).

When in solution, test with iron salts (193).

For solubilities, ferrocyanides, see 629; ferricyanides, 632; sulphocyanates, see 642. The Cy of single cyanides is separated by slightly acidulating, adding calcium carbonate, and distilling—ferrocyanogen and ferricyanogen and sulphocyanogen being retained as salts.

Concerning the Removal of Bases, before Testing for Acids, see 769.

Heat a portion of the neutralized solution, and add both* **barium chloride** *and* **calcium chloride.**

Precipitate; $BaSO_4$, CaC_2O_4, $CaHPO_4$, or $Ca_3(PO_4)_2$, etc. Also, barium and calcium **borates, silicates, fluorides** (744), **ferrocyanides, sulphites, chromates, arseniates, iodates**—the acids of which will be identified by 800, or during the work for bases. Also, **tartrates** (758), citrates (762), and salts of other organic acids not described in this work. Concerning Selenates, Tellurites, see **499**; Molybdates, 495.

Digest the precipitate with dilute **hydrochloric acid.** If a precipitate remains, filter.

Residue; $BaSO_4$ (white).
See 676.
Sulphates precipitate lead and strontium salts.
For comparison of the chief reactions, see 720.

Solution; $H_2C_2O_4$; H_3PO_4 or $CaH_4(PO_4)_2$, etc.; barium and calcium chlorides; other acids of less frequent occurrence, as indicated above.

Add **ammonium hydrate** *to a slight alkaline reaction.*

Precipitate; CaC_2O_4, $CaHPO_4$, etc.

Add **acetic acid** *to a distinctly acid reaction.*

Residue; CaC_2O_4 (white).
See 656.
Reactions compared in 720.
Preliminary examination for acids, 800, Test I., Result 1.

Solution; $CaH_4(PO_4)_2$, etc. (707).

Add ammonium hydrate to a slight alkaline reaction.

Precipitate; $CaHPO_4$.

Filter and wash, and dissolve by acetic acid.

Test by **molybdate,** as directed in 714.

Or, *add potassium acetate, neutralize any excess of acid by adding* **KOH,** *leaving the reaction acid, and precipitate by* **ferric chloride.** Precipitate; $Fe_2(PO_4)_2$ (711). This precipitate, dissolved by **HCl**; then treated with tartaric acid (133), excess of **ammonia**, and **magnesium sulphate,** gives the *ammonium magnesium phosphate,* $MgNH_4PO_4$.

Reactions compared, 720.

* For Sulphuric acid, the reaction may be acid; for oxalic acid, the solution may have acetic acidulation; but for phosphoric acid, it must not have an acid reaction. Acidity should be neutralized by ammonium hydrate, which may be added in slight excess.

To the neutral or slightly acid solution, add* **silver nitrate.**

Precipitate: Silver salts of a very large number of acids, including those in the residue next below, together with silver carbonate, sulphide, tartrate, and other precipitates dissolved by nitric acid (328).

Digest with dilute hot **nitric acid.**

Residue: AgCl, AgBr, AgI, AgCy, $AgIO_3$, $AgBrO_3$, AgCyS.

Add **Ammonium Hydrate** *to a strong alkaline reaction* (577).

Residue: AgI, indicating **Iodides.**

Test the original solution for iodides, by chlorine water with carbon disulphide (or starch), as directed in 565.

Follow the **Table** *at page* 173, *and consult the text at* 576 *and at* 556.

Solution: Ammonia silver compounds, representing **HCl, HBr, HCy, $HBrO_3$, HIO_3, HCyS.**

Add dilute **nitric acid** *to a slight acidulation.*

Precipitate: AgCl, AgBr, AgCy, $AgIO_3$, $AgBrO_3$, AgCyS.

Test the original solution for **chloride.**

By distillation for chlorinated chromic anhydride (512).

By the solubilities of the silver precipitate in ammonium hydrate and carbonate (509)

Test the original solution for **bromide,** *as directed in* 539 *and in* 576.

Test the original solution for **iodate,** *by reducing agents* (571), *and by precipitations* (574).

Test the original solution for **bromate,** *as directed in* 547.

Test the original solution for cyanide, 621 *or* 622.

Test the original solution for **sulphocyanate,** by 642. Observe 643.

Follow the Table of Comparative Reactions, at page 173, and for **HCy,** at page 202.

* If alkaline, the solution should be neutralized by nitric acid. Should effervescence result, boil until it is complete. Should a precipitate form, remove it by filtration.

PART IV.

OXIDATION.

BY OTIS COE JOHNSON, M.A.

806. In this part is described the oxidizing and reducing action of the following substances upon each other:

811. $H_2C_2O_4$	827. I	843. As'''
812. H_2CO_3	828. HI	844. As^{V}
813. HNO_2	829. HIO_3	845. Bi'''
814. HNO_3	830. HCy	846. Cu''
815. H_3PO_2	831. HCyS	847. Mn''
816. H_3PO_4	832. H_4FeCy_6	848. Mn''''
817. H_2S	833. H_3FeCy_6	849. Mn^{VII}
818. H_2SO_3	834. Pb''	850. Co''
819. H_2SO_4	835. Pb''''	851. Co'''
820. Cl	836. Ag'	852. Ni''
821. HCl	837. Hg'	853. Ni'''
822. HClO	838. Hg''	854. Fe''
823. $HClO_3$	839. Sn''	855. Fe'''
824. Br	840. Sn''''	856. Cr'''
825. HBr	841. Sb'''	857. Cr^{VI}
826. $HBrO_3$	842. Sb^{V}	

In this list the acids are arranged in order of the atomic weight of the element, which suffers oxidation or reduction, in each. The bases are arranged in accordance with the usual analytical grouping. In all cases, to avoid repetition, the action of any substance is given upon those which *follow* it and never upon those which precede it in the list. To express the bonds of the bases accents are employed, and the action stated is true of all salts, oxides, or hydrates of the metal having the stated number of bonds.

807. NEGATIVE BONDS. I am compelled to use the word *bond* in a sense perhaps original; at any rate I give to this word an additional meaning entirely different from that of all authors heretofore. By the *bond* of an element is meant, the amount of oxidation it is capable of sustaining. A bond, then, may be defined as *oxidizing force, and when an element has no oxidizing force or power, it has no bonds*, and when its only capacity is that of a *reducing* agent, its bonds are represented by a negative number.

808. The bonds of an element may always be ascertained with certainty by one or more of the following rules:

1st. Hydrogen, in combination, has always one bond, and it is always positive (H′).

2d. Oxygen always has two bonds, and they are always negative (or minus) ($O^{-''}$).

3d. Free elements have no bonds; thus, metallic lead (Pb^{o}).

4th. The sum of the bonds of any compound is always equal to zero. Thus, $H'N^{+v}O_3^{-vi=o}$; that is, the H has one positive bond, the N five positive bonds, and each atom of O has two negative bonds, and the three atoms have six negative bonds—six positive bonds added to six negative bonds equal zero. In the same way, $H'Cl^{+v}O_3^{-vi=o}$, $H_2''S^{+vi}O_4^{-viii=o}$, $H_3'''P^{+v}O_4^{-viii=o}$, $Ba''O_2^{-''''}H_2^{+''=o}$, $Fe_2^{vi}O_6^{-xii}H_6^{+vi=o}$, $Ba''H_4^{+''''}P_2^{+x}O_8^{-xvi=o}$.

5th. Acid radicals are always negative. $H'I^{v}O_3^{-vi=o}$, or $H'(IO_3)^{-'=o}$, $Pb_3^{vi}P_2^{+x}O_8^{-xvi=o}$, or $Pb_3^{vi}(PO_4)_2^{-vi=o}$. The bonds of the radical being equal to the number of atoms of hydrogen with which it is capable of combining.

6th. Metals in combination are usually positive. The most prominent exceptions are their compounds with hydrogen, $Sb^{-'''}H_3^{+'''}$, $As^{-'''}H_3^{+'''}$.

809. An *oxidizing agent* is one that can increase the number of bonds of some other substance.

A *reducing agent* is one that can diminish the number of bonds of some other substance.

Hence oxidation of one substance *must* involve the reduction of some other. The number of bonds gained by one are lost by the other.

The real bonds are transferred from the oxidizing to the reducing agent. Thus, in the equation

$$2PbCrO_4 + 5Zn + 16HCl = 2Pb + Cr_2Cl_6 + 5ZnCl_2 + 8H_2O$$

it can be proven that the ten bonds lost by the lead chromate are transferred to the zinc.

810. From these principles is derived a rule for writing equations, by which every equation involving oxidation may be balanced almost at a glance, if we know the products formed. The rule is: **The number of bonds changed in one molecule of each shows how many molecules* of the other must be taken,** the words *each* and *other* referring respectively to oxidizing and reducing agent. A few equations will illustrate:

$$2HNO_3 + 3H_2SO_3 = 3H_2SO_4 + 2NO + H_2O$$

The nitrogen in HNO_3 has five bonds, and in NO it has two, losing three; therefore, three molecules of H_2SO_3 must be taken. The sulphur in H_2SO_3 has four bonds, and in H_2SO_4 it has six, gaining two; therefore, two molecules of HNO_3 must be taken. Again:

$$3Sn^* + 4HNO_3 = 3SnO_2 + 4NO + 2H_2O$$

The Sn gains four bonds (free elements having no bonds), hence four molecules of HNO_3 must be taken, and the N of the HNO_3 losing three bonds, three of Sn must be taken.

$$6Sb + 10HNO_3 = 3Sb_2O_5 + 10NO + 5H_2O$$

Here the rule calls for three of Sb and five of HNO_3; but since the product, Sb_2O_5, cannot be written with an odd number of atoms of antimony, we must double the number of each, and, instead of three and five, take six and ten.

$$3H_2S + 8HNO_3 = 3H_2SO_4 + 8NO + 4H_2O$$

Here the sulphur in H_2S has -2 (minus two) bonds, and in H_2SO_4 it has $+6$, so it has gained eight bonds; hence we must take eight molecules of HNO_3, and we take three of H_2S because the nitrogen loses three bonds.

$$3Sb_2S_3 + 28HNO_3 = 3Sb_2O_5 + 9H_2SO_4 + 28NO + 5H_2O$$

In this equation both the sulphur and the antimony of the Sb_2S_3 are oxidized, each atom of sulphur gains eight bonds (as explained above), and the three atoms will gain twenty-four bonds. Each atom of antimony gains two bonds, the two atoms gaining four bonds; these added to the twenty-four bonds gained by the sulphur make twenty-eight (that is, one molecule of Sb_2S_3 gains twenty-eight bonds); hence we must take twenty-eight molecules of HNO_3, also three of Sb_2S_3, because the nitrogen loses three bonds.

* In case of free elements, to avoid complexity, atoms are represented as molecules.

$$HIO_3 + 3H_2SO_3 = 3H_2SO_4 + HI$$

In this the rule calls for two of HIO_3 and six of H_2SO_3; but we take one and three, which are in the same proportion. The rule gives proportional numbers only.

$$3Pb + 2+6HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O$$

Here the rule requires two of HNO_3, and shows that just two are reduced to **NO**; but in order to make a solution of lead nitrate six more must be added, which are not reduced.

$$3NaH_2PO_2 + 7HNO_3 = 3NaNO_3 + 3H_3PO_4 + 4NO + 2H_2O$$

Here the phosphorus gains four bonds and four of HNO_3 are reduced to **NO**; but three more are required to liberate the hypophosphorous acid from $3NaH_2PO_2$; hence we take seven in all.

$$AsH_3 + 6AgNO_3 + 3H_2O = 6Ag + H_3AsO_3 + 6HNO_3$$

The arsenic in AsH_3 has —3 bonds, and in H_3AsO_3 it has +3; the gain is six; therefore, take six of $AgNO_3$.

$$3KNO_3 + 8Al + 5KOH + 2H_2O = 3NH_3 + 4K_2Al_2O_4$$

The nitrogen in NH_3 has —3 bonds, having lost eight; therefore, take eight of **Al**; and as the **Al** gains three, take three molecules of KNO_3.

OXALIC ACID.

811. *a.* The carbon in oxalic acid ($H_2C_2O_4$) has three bonds. In presence of water, reducing agents have no action upon it. By fusion, however, a few metals, **K**, **Na**, **Mg**, etc., reduce it to free carbon.

HNO_2 *b.* Nitrous acid seems to have no action on oxalic.

HNO_3 *c.* **NO** is formed, and the oxalic becomes CO_2 [*Gmelin's Hand-book*, 9, 116].

Experiment: To dry oxalic acid add nitric acid, sp. gr. 1.42, or, better, 1.50. Test the evolved gas for **NO** by 814, and for CO_2 by passing it into a solution of barium chloride containing free potassium hydrate.

Cl *d.* **HCl** is formed, and the oxalic becomes CO_2 [*Gmelin's Hand-book*, 9, 116]. The CO_2 is tested (811 *c*); then prove the absence of free **Cl** by **KI**, and of **HCl** by $AgNO_3$. This change of bonds takes place more readily in presence of potassium hydrate.

HClO *e.* Forms CO_2 and **Cl** [*Watts' Dictionary of Chemistry*, 4, 250; *Wurtz's Dictionnaire de Chimie*, 2, 670]. If the oxalic acid is in excess, **HCl** is formed. Proof, same as above. The action is more rapid in presence of fixed alkali.

$HClO_3$ *f.* Forms CO_2 and varying proportions of Cl_2O_4, **Cl**, and **HCl**. A high degree of heat and excess of oxalic acid favoring the production of **HCl** [*Calvert and Davies, Jour. Chem. Society*, II. 193]. To prove CO_2, pass the gas into a solution of barium hydrate, or a mixture of barium chloride and potassium hydrate.

Br *g.* Does not decompose oxalic acid [*Schönbein, Jour. für Praktische Chemie*, 88, 469].

Does decompose oxalic acid [*Wurtz's Dictionnaire de Chimie*, 2, 671].

Does decompose in alkaline mixture [*A. Cahours, Annales de Chimie*, III. 19, 486; *Jour. für Praktische Chemie*, 41, 61].

It has not been clearly proven that any action takes place, except in presence of fixed alkali.

$HBrO_3$ *h.* Bromine and CO_2 are formed.

HIO_3 *i.* Forms CO_2 and **I** [*H. Davy*].

Add the acid and test for CO_2 by calcium hydrate, and for **I** by carbon disulphide.

The following acids do not change the bonds of oxalic acid: Carbonic, phosphoric, hypophosphorous, hydrosulphuric, sulphuric (but see 653), hydrochloric, hydrobromic, hydriodic, hydrocyanic, sulphocyanic, hydroferricyanic, hydroferrocyanic.

Pb″″ *k.* PbO_2 with oxalic acid forms **Pb″** and CO_2 [*Gmelin's Hand-book*, 9, 118; *Watts' Dictionary of Chemistry*, 4, 250].

Oxalic acid has no action upon Pb_3O_4.

Hg″ *l.* Oxalate of ammonia boiled in the sunlight gives Hg_2Cl_2 and CO_2 [*Gmelin's Hand-book*, 9, 118; *Watts' Dictionary of Chemistry*, 4, 251].

Free oxalic acid boiled in the sunlight also gives Hg_2Cl_2.

As^v *m.* H_3AsO_4 becomes H_3AsO_3, and CO_2 is evolved.

To prove that **As^v** becomes **As‴**, add excess of potassic hydrate, and then potassic permanganate. The latter will be quickly decolored.

Mn″″ *n.* Forms **Mn″** and CO_2.

Mn^{VII} *o.* Forms **Mn″** and CO_2.

Co''' *p.* Becomes Co'' and CO_2.

Ni''' *q.* Forms Ni'' and CO_2.

Cr *r.* Rapidly forms Cr''' and CO_2.

CARBONIC ACID.

812. The carbon of carbonic acid cannot be further oxidized, and is not reduced in presence of water. It is, however, changed to free carbon by fusing with metallic potassium, sodium, and even magnesium.

NITROUS ACID.

813. Nitrous acid acts sometimes as an oxidizing and sometimes as a reducing agent. When it oxidizes nitric oxide is formed. When it reduces nitric acid is produced.

H_3PO_2 *b.* Nitric oxide and phosphoric acid are formed.

Prove by silver nitrate, or treat calcium hypophosphite with potassium nitrite and hydrochloric acid, then add ammonium hydrate, and a precipitate will show that calcium phosphate is formed.

H_2S *c.* Forms sulphur and ammonium nitrate [*Gmelin-Kraut, Handbuch der Chemie*, I. 2, 458; *Wurtz's Dictionnaire de Chimie*, I. 489].

Hydrosulphuric acid has no action upon nitrite of potassium, but on addition of acetic acid sulphur separates, and if the solution is hot nitric oxide is formed, the fumes of peroxide of nitrogen being clearly visible. Keeping the mixture cold favors the formation of ammonium nitrate.

H_2SO_3 *d.* Forms sulphuric acid and nitric oxide [*Gmelin-Kraut, Handbuch der Chemie*, I. 2, 458].

Traces of ammonium nitrate are also formed [*Frémy*].

$HClO_3$ *g.* First forms peroxide of chlorine, Cl_2O_4 [*Millon*], then hydrochloric acid [*Toussaint; Gmelin-Kraut, Handbuch der Chemie*, I. 2, 458].

Add chloric acid to potassium nitrite; then addition of silver nitrate shows that hydrochloric acid is formed.

Br *h.* Free bromine seems to have no action on nitrous acid.

HI *j.* Forms iodine and nitric oxide [*Watts' Dictionary*, 4, 71; *Wurtz's Dictionnaire de Chimie*, I. 489].

HIO_3 *k.* Forms iodine and nitric acid.

HCyS *l.* Forms sulphuric and hydrocyanic acids, and nitric oxide. Sometimes traces of other cyanogen products are formed.

H_4FeCy_6 *m.* Forms first, hydroferricyanic acid, then nitroferricyanic acid.

H_3FeCy_6 *n.* Forms nitroferricyanic acid.

PbO_2 *o.* Forms Pb″ and nitric acid [*Gmelin-Kraut, Handbuch der Chemie*, I. 2, 458].

Hg′ *p.* Becomes Hg^0 [*Watts' Dictionary*, 4, 70; *Wurtz's Dictionnaire de Chimie*, I. 489; *Gmelin-Kraut, Handbuch der Chemie*, I. 2, 460].

Mercuric salts are not reduced [*Heppe, Chemische Reactionen*, 336].

Mn‴′ *q.* Forms Mn″ [*Gmelin-Kraut, Handbuch der Chemie*, I. 2, 458].

Mn^{VII} *r.* Forms Mn″ and nitric acid [*Gmelin-Kraut, Handbuch*, I. 2, 458].

Co″ *s.* Changes Co″ to Co‴ (225) [*Watts' Dictionary*, I. 1045].

Ni‴ *t.* Nitrites acidulated with phosphoric acid reduce Ni‴ to Ni″ in the cold.

Cr^{VI} *u.* Becomes Cr‴ [*Watts' Dictionary*, 4, 70].

NITRIC ACID.

814. *a.* Of course nitric acid can never act as a reducing agent. Acting as an oxidizing agent, it may form NH_3, N, N_2O, NO, N_2O_3, or N_2O_4.

If the nitric acid is in excess, and a boiling heat be used, the product is nearly all NO, while excess of the reducing agent and a low temperature favor the formation of NH_3.

A convenient test for NO is made by passing the gas into ferrous sulphate. (See 590 and *Acworth and Armstrong, Jour. Chem. Society*, 32, 54.)

H_3PO_2 *b.* Becomes phosphoric acid.

Experiment: Treat with nitric acid until it no longer blackens argentic nitrate, and when mixed with ammonium hydrate, gives a precipitate with chloride of calcium.

H_2S *c.* Forms sulphur, and may be further oxidized to sulphuric acid. The nitric acid must be stronger than sp. gr. 1.18 [*Gmelin-Kraut, Handbuch*, I. 2, 219).

H_2SO_3 *d.* Becomes sulphuric acid.

HCl *e.* Forms nitrohydrochloric acid (513).

$HClO_3$ *f.* Nitric acid added to a chlorate liberates chloric acid, which decomposes, but the nitric is not changed [*Penny, Jour. Prakt. Chem.*, 23, 296].

HBr *g.* Gives free bromine.

I *h.* Forms iodic acid; action slow, and strong nitric acid should be used—at least sp. gr. 1.42. This is a practical method for making iodic acid, if acid of sp. gr. 1.48 is used [*Bousson, Comptes Rendus Academie des Sciences*, 13, 1111].

HI *i.* Forms first free iodine, then iodic acid.

HCyS *j.* Forms hydrocyanic and sulphuric acids.

With strong nitric acid, traces of carbonic acid are formed [*Vögel, Gmelin's Hand-book*, 8, 75].

H_4FeCy_6 *k.* Forms hydroferricyanic acid [*Watts' Dictionary*, 2, 250], and then nitroferricyanic acid.

H_3FeCy_6 *l.* Forms nitroferricyanic acid. Proof: Test by adding some soluble sulphide (668).

m. Nitric acid oxidizes all ordinary metals. (It does not act upon gold or platinum.) It forms nitrates, except in the case of tin and antimony, with which it forms the insoluble oxides, **SnO_2** and **Sb_2O_5**.

With the respective metals it forms **Hg′** or **Hg″**, **Sn″** or **Sn⁗**, **As‴** or **As^v**, **Sb‴** or **Sb^v**, **Fe″** or **Fe‴**, according to the amount of nitric acid employed.

With copper it forms cupric nitrate (never cuprous); with cobalt it forms cobaltous nitrate.

Pb_3O_4 *n.* Becomes plumbic nitrate and **PbO_2**. The nitric acid is not reduced.

Hg′ *o.* Becomes **Hg″**.

SnO *p.* Becomes **SnO_2**. (Not stannic nitrate.)

Prove by adding **$KMnO_4$** to alkaline solution, after treating with nitric acid.

H_3AsO_3 *q.* Becomes **H_3AsO_4**. Prove as above.

Sb_2O_3 *r.* Becomes **Sb_2O_5**. Prove as above.

Cu′ *s.* Becomes **Cu″**.

t. **MnO, NiO, CoO, Cr_2O_3** are not oxidized.

Fe″ *u.* Becomes **Fe‴**.

HYPOPHOSPHOROUS ACID.

815. *a.* Tests for hypophosphorous acid are given in 721 to 725. Perhaps the best method of proving that H_3PO_2 is all changed to H_3PO_4, is that it fails to blacken argentic nitrate. The reduction of mercuric chloride is sometimes preferred, especially if hydrochloric acid is present.

Where the oxidation is not fully complete, first remove any phosphate which may be present as an impurity, by addition of magnesium sulphate in presence of ammonium chloride and ammonium hydrate; then, after oxidation, repeat the process to prove partial oxidation.

H_2SO_3 *b.* Becomes chiefly free sulphur, but if the hypophosphorous acid is in great excess traces of hydrosulphuric acid are formed.

H_2SO_4 *c.* Becomes first sulphurous acid, then sulphur [*Wurtz's Dictionnaire de Chimie*, 2, 968].

Cl *d.* Becomes hydrochloric acid, and phosphoric acid is formed. Prove the absence of free chlorine by potassium iodide, and formation of hydrochloric acid by argentic nitrate.

HClO *e.* Becomes hydrochloric acid. Prove same as above.

$HClO_3$ *f.* Becomes hydrochloric acid. Prove same as above.

Br *g.* Forms hydrobromic acid. Prove absence of bromine by potassium iodide, and formation of hydrobromic acid by argentic nitrate.

The action takes place also in alkaline mixture.

$HBrO_3$ *h.* Forms hydrobromic acid. Prove same as above.

I *i.* Forms hydriodic acid.

Prove absence of free iodine, by loss of color, with carbon disulphide and prove presence of hydriodic acid by chlorine.

HIO_3 *j.* Forms hydriodic acid.

Prove absence of iodic by sulphurous acid with carbon disulphide, and formation of hydriodic acid as above.

H_4FeCy_6. *k.* Forms hydroferrocyanic acid. In this case the formation of the same cannot be proven by addition of ferric chloride, because an excess of hypophosphorous acid changes ferric chloride to ferrous chloride, which then gives a precipitate with ferricyanide of potassium. A good method is to add a slight excess of fixed alkali, and then an excess of alcohol which will precipitate the ferrocyanide of potassium, which may, after washing with alcohol, be dissolved in water and tested in the usual way.

Pb''' *l.* Becomes Pb'' both in presence of fixed alkali and acids.

Ag' *m.* Becomes Ag^{o} " " " "

Hg' *n.* Becomes Hg^{o} " " " "

Hg'' *o.* Becomes Hg^{o} " " " "

As^{v} and As''' *p.* Become metallic arsenic (in presence of acids only).

Bi''' *q.* Becomes Bi''. The action takes place both in presence of alkalies and acetic acid.

Cu'' *r.* Becomes Cu'. The action occurs in presence of hydrochloric acid. Proof: Changes from green to colorless, and on addition of ammonium hydrate makes colorless solution.

Mn'''' *s.* In presence of acids gives Mn''. (No action in presence of alkalies.)

Mn^{VII} *t.* With alkalies gives Mn^{IV}.
With acids gives Mn''.

Co''' *u.* Becomes Co''. No action in alkaline mixture.

Ni''' *v.* Becomes Ni''. " "

Fe''' *w.* Becomes Fe''. " "

Cr^{VI} *x.* Becomes Cr'''. " "

PHOSPHORIC ACID.

816. Phosphoric acid in presence of acids is not reduced. By fusing with metallic magnesium P_2Mg_3 is formed, which, on being treated with water, forms MgO and PH_3 [*Jour. Chem. Society, Blunt*, 18, 106; *Parkinson*, 20, 309].

HYDROSULPHURIC ACID.

817. *a.* Free sulphur liberated from hydrosulphuric acid may sometimes be recognized simply by its appearance. But when white precipitates are formed at the same time, the whole should be allowed to settle, then the sulphur dissolved in carbon disulphide, and again separated by evaporation, or precipitated from the carbon disulphide solution by addition of alcohol, and then further tested by 659, 662.

H_2SO_3 *b.* Forms water and sulphur [*Watts' Dictionary*, 3, 203].

Sometimes, especially if the moist gases are used, pentathionic acid, $H_2S_5O_6$, is formed. $5SO_2 + 5H_2S = H_2S_5O_6 + 4H_2O + 5S$. E. Pfeiffer [*Archiv der Pharmacie* (3), 14, 344; *Jour. Chem. Society*, 36, 1013] claims to have proven that tetrathionic acid, $H_2S_4O_6$, is formed, instead of pentathionic.

H_2SO_4 *c.* No action if the sulphuric acid is dilute.

With strong acid, sulphur and sulphurous anhydride are formed. To prove the latter, add sulphuric acid to dry ferrous sulphide and boil, or pass hydrosulphuric acid gas into hot sulphuric acid, and SO_2 will be evolved.

Cl *d.* Forms first sulphur, and finally sulphuric and hydrochloric acids. This takes place in alkaline mixture also.

HClO *e.* Same as above.

$HClO_3$ *f.* With excess of hydrosulphuric acid, free sulphur and hydrochloric acid are formed.

With excess of chloric, sulphuric acid and chlorine are formed.

Br *g.* Forms hydrobromic acid and sulphur [*Watts' Dictionary*, 3, 203]. In alkaline mixture sulphuric acid is also formed.

$HBrO_3$ *h.* Forms sulphur and hydrobromic acid. Sulphuric acid is also formed [*Rose; Heppe, Chemische Reactionen*, 75].

I *i.* Forms sulphur and hydriodic acid.

HIO_3 *j.* With excess of hydrosulphuric acid, hydriodic acid and sulphur are formed.

With excess of iodic distinct traces of sulphuric acid are formed.

H_3FeCy_6 *k.* Forms potassium ferrocyanide and sulphur.

Proof: Boil to expel excess of hydrosulphuric acid, then add ferric chloride.

PbO_2 *l.* Forms PbS and sulphur. Test for sulphur by 817 *a*, and for PbS, after washing with water, add zinc and hydrochloric acid, when hydrosulphuric acid will be evolved.

To prove that no PbO_2 remains, after washing add potassium iodide and carbon disulphide. If any PbO_2 is present, free iodine will be formed.

As^v. As_2S_3 and free sulphur are formed.

Mn'''' *m.* Forms manganous sulphide and sulphur, changing from black to flesh color.

Mn^{VII} *n.* With potassium sulphide, potassium sulphate is formed [*M. Schlagdenhafen, Bulletin de la Société Chimique* (2), 22, 16; and *Jour. Chem. Society*, 28, 912]. $8KMnO_4 + 3K_2S = 3K_2SO_4 + 4K_2O + 8MnO_2$. This method he uses quantitatively for the estimation of hydrosulphuric acid. With some free acid, such as phosphoric, hydrosulphuric added in excess to potassium permanganate gives manganous sulphide and free sulphur.

H_2CrO_4 *o.* Forms chromic oxide and sulphur [*Gmelin's Hand-book*, 2, 119, and 4, 119].

Ni_2O_3 *p.* Becomes nickelous sulphide and sulphur. Proof, same as for 817 *l.*

Co_2O_3 *q.* Forms cobaltous sulphide and sulphur. " " "

Fe''' *r.* Forms Fe'' and sulphur. The action takes place in either alkaline or acid mixture.

SULPHUROUS ACID.

818. *a.* Upon other acids sulphurous acid acts as a reducing agent, except with hypophosphorous and hydrosulphuric acids, 815–817. With free metals it acts only as an oxidizing agent. With metallic oxides it is a reducing agent, except with stannous oxide. The method of proof is, in all cases, very simple.

Cl *b.* Forms sulphuric and hydrochloric acids.

HClO *c.* " " " "

$HClO_3$ *d.* " " " "

Br *e.* " " hydrobromic "

$HBrO_3$ *f.* Forms first bromine, then sulphuric and hydrobromic acids.

I *g.* Forms hydriodic and sulphuric acids.

HIO_3 *h.* Forms first iodine, then hydriodic and sulphuric acids.

H_3FeCy_6 *i.* According to Boudault [*Jour. Prakt. Chem.*, 36, 23] and many other authorities, potassium ferrocyanide and sulphuric acid are formed. Their method of proof is not clear.

PbO_2 *j.* Forms plumbic sulphate [*Heppe, Chemische Reactionen*, 315].

Ag' *k.* Forms metallic silver.

Hg' and Hg'' *l.* With the nitrates of mercury, metallic mercury is formed. With mercuric chloride, mercurous chloride is very slowly precipitated.

Sn″ *m.* With stannous chloride, forms stannic sulphide, or stannic chloride and hydrosulphuric acid, according to the amount of hydrochloric acid present.

As^{v} *n.* Forms arsenious and sulphuric acids.

MnO_2 *p.* If the solution is hot, manganous sulphate is formed [*Watts' Dictionary*, 5, 636]. If cold, manganous dithionate, **MnS_2O_6**, is formed [*Gmelin's Hand-book*, II. 174].

Co_2O_3 *q.* Forms **Co″**.

Ni_2O_3 *r.* Forms **Ni″**.

Fe‴ *s.* Forms **Fe″**.

Cr^{VI} *t.* Forms chromic sulphate.

SULPHURIC ACID.

819. *a.* Sulphuric acid can of course never act as a reducing agent, and it does not oxidize the other acids, except hypophosphorous (815 *c*), hydrobromic, and hydriodic acids. Some others are decomposed, but not oxidized, and the sulphuric is not reduced.

HBr *b.* Forms bromine and sulphurous acid. No action occurs except in concentrated solution.

HI *c.* Forms iodine and sulphurous acid.

d. Metals, when dissolving in dilute sulphuric acid, evolve hydrogen, and form sulphates.

When the metals dissolve in strong sulphuric acid, **SO_2** is evolved, and sulphates are formed.

Dilute sulphuric acid does not oxidize any of the metallic oxides. *Concentrated* acid changes the following.

Hg_2O *e.* Forms mercuric sulphate, and sulphurous anhydride is evolved.

SnO *f.* Stannous chloride forms first, sulphurous anhydride, then hydrosulphuric acid, stannic chloride at the same time being produced. Compare 818 *m*.

Mn *g.* With the higher oxides of manganese, dilute sulphuric acid has no action. Concentrated, boiling solutions evolve oxygen and manganous sulphate is formed.

CHLORINE.

820. *a.* The most delicate test for chlorine is potassium iodide with carbon disulphide (557). If, however, other oxidizing agents are present, the test must be varied to avoid error.

Chlorine is one of the strongest oxidizing agents, becoming always hydrochloric.

HBr *b.* Forms bromine and hydrochloric acid.

I *c.* Forms iodic and hydrochloric acids. In presence of potassium hydrate, potassium periodate is formed.

HI *d.* Forms first iodine, then iodic acid. With potassium hydrate, same as above.

HCyS *e.* Forms first a red compound of unknown composition, then hydrocyanic, sulphuric, and hydrochloric acids.

H_4FeCy_6 *f.* Forms first hydroferricyanic and hydrochloric acids. Excess of chlorine to be avoided in preparation of ferricyanides.

H_3FeCy_6 *g.* Decomposes, forming various products.

h. Chlorine unites with all metals, forming chlorides. If any metal is capable of forming two series of salts, it always changes the one in which the metal has the less number of bonds, to that having the greater. That is, it changes *ous* salts to *ic*.

Especially in the presence of a fixed alkali, it changes nearly all the lower oxides and hydrates to the highest the metal is capable of forming. Among the ordinary metals, the only exceptions are peroxide of silver, and the peroxides of the alkalies and alkaline earths.

i. By comparing this with 824 and 827, the following facts will be observed, and should be carefully considered. The elements, chlorine, bromine and iodine have an oxidizing power in order of their combining numbers, chlorine being the strongest. This rule has no exceptions.

Their hydracids are reducing agents graded in the reverse order.

If any increase of bonds takes place in presence of an acid, by chlorine, bromine, or iodine, the same increase always occurs in presence of a fixed alkali. But the oxidation frequently goes further in presence of a fixed alkali. Thus, with chlorine and potassium hydrate we form PbO_2, Ni_2O_3, Bi_2O_5, Co_2O_3, K_2FeO_4, MnO_2, and $KMnO_4$, which cannot be formed in presence of an acid.

It is very important to remember that *those oxides which are formed by chlorine, in presence of a fixed alkali, but not in presence of an acid, are the only ones which can be reduced by hydrochloric acid. And further, that this reduction proceeds not always to the original form, never proceeding beyond that number of bonds capable of being formed in presence of an acid.* Thus, any plumbic salt, with potassium hydrate and chlorine, forms PbO_2, and this treated with hydrochloric acid again forms the plumbic salt $PbCl_2$. And ferrous chloride with potassium hydrate and chlorine forms K_2FeO_4, in which iron is a true hexad, and K_2FeO_4 with hydrochloric acid forms, not the ferrous chloride with which we began, but ferric chloride, for it could be oxidized to that point in presence of an acid.

The above rule is true for bromine and iodine as well as for chlorine.

Pb'' *j*. Becomes PbO_2, with fixed alkalies, not in acid solution.

$$PbO + 2KHO + Cl_2 = PbO_2 + 2KCl + H_2O$$

$$Pb(NO_3)_2 + 4KHO + Cl_2 = PbO_2 + 2KNO_3 + 2KCl + 2H_2O$$

$$Pb_3(PO_4)_2 + 12KHO + Cl_6 = 3PbO_2 + 2K_3(PO_4) + 6KCl + 6H_2O$$

Hg' *k*. Becomes Hg'' in acid and in alkaline mixture.

Sn'' *l*. Becomes Sn'''' " " "

$$K_2SnO_2 + 2KHO + 2Cl = K_2SnO_3 + 2KCl + H_2O$$

As''' *m*. Becomes As^V in acid and alkaline mixture.

Sb''' *n*. Becomes Sb^V " " "

Bi''' *o*. Becomes Bi^V in alkaline mixture only.

$$2BiCl_3 + 10KHO + 4Cl = Bi_2O_5 + 10KCl + 5H_2O$$

Mn'' *p*. Becomes MnO_2 in alkaline mixture only, and after passing the chlorine gas for three or four hours a large portion becomes $KMnO_4$.

Co'' *q*. Becomes Co_2O_3 in alkaline mixture only.

Ni'' *r*. Becomes Ni_2O_3 " " "

Cr''' *s*. Becomes Cr^{VI} (a chromate) in alkaline mixture only.

Fe'' *t*. Becomes Fe''' in alkaline and acid mixture, but is further oxidized to K_2FeO_4 only in alkaline mixture.

HYDROCHLORIC ACID.

821. For some properties of hydrochloric acid consult 820 *a*.

$HClO$ *a*. Forms chlorine and water. $HClO + HCl = Cl_2 + H_2O$.

$HClO_3$ *b.* Gives chlorine, and a varying amount of the several oxides of chlorine [*Storer's Quantitative Analysis*, 119].

$HBrO_3$ *c.* In very dilute solution, no action.

HIO_3 *d.* In dilute solution, no action. If concentrated, yellow chloride of iodine is formed, not taken up by carbon disulphide.

e. In all cases where metals are dissolved in hydrochloric acid, hydrogen is evolved. In such cases it is an oxidizing agent, the chlorine of the acid not changing its bonds, but the hydrogen is changed from combined, in which it is plus, to free hydrogen, where it has no bonds, thereby losing one bond.

For its action on oxides see 820 *i.*

Pb_3O_4 and PbO_2 *f.* Form plumbic chloride and chlorine.

Mn *g.* All compounds of manganese having more than two bonds are reduced to the dyad, with evolution of chlorine. If the solutions are dilute this change is preceded by formation of manganese peroxide [*S. U. Pickering, Jour. Chem. Society*, 35, 654].

Co and **Ni** *h.* Cobaltic and nickelic oxides are changed to cobaltous and nickelous chlorides, with evolution of chlorine.

Fe^{VI} *i.* With the exception of ferrates, as K_2FeO_4, which forms ferric chloride, the compounds of iron are not reduced.

Cr^{VI}. Forms chromic chloride, and chlorine is evolved.

HYPOCHLOROUS ACID.

822. The oxidizing power of this acid is, in general, the same as that of free chlorine.

CHLORIC ACID.

823. *a.* Chloric acid for the following operations may be easily made, by adding to barium chlorate just enough sulphuric acid to precipitate all the barium as a sulphate.

It is a strong oxidizing agent, becoming free chlorine mixed with various oxides of chlorine. If the reducing agent is used in excess, hydrochloric acid is the final product, but in the operation much of the chlorine escapes into the air.

HBr *b.* Forms bromine.

I *c.* Forms iodic acid.

HI *d.* Forms first iodine, then iodic acid.

$HCyS$ *e.* Forms first a red compound of unknown composition, then hydrocyanic and sulphuric acids.

H_4FeCy_6 *f.* Forms first hydroferricyanic acid, which may be further oxidized.

H_3FeCy_6 *g.* Chloric acid acts upon potassium ferricyanide, forming potassium superferricyanide, K_2FeCy_6.

$$6K_3FeCy_6 + KClO_3 + 6HCl = 6K_2FeCy_6 + 7KCl + 3H_2O$$

[*Z. H. Skraup, Liebig's Annalen der Chemie*, 189, 368]. In this salt the iron has four bonds.

Sn'' *h.* Forms Sn''''. Proof: After adding excess of potassic hydrate it does not decolor potassium permanganate.

AS''' *j.* Forms arsenic acid. Proof, same as above.

Fe'' *l.* Becomes Fe'''.

BROMINE.

824. *a.* Bromine as an oxidizing agent is intermediate in strength between chlorine and iodine. In presence of acids it never acts as a reducing agent. In oxidizing it becomes $Br^{-\prime}$; that is, hydrobromic acid or a bromide.

The tests for hydrobromic acid are given in 532, 541.

A good method of proving the absence of free bromine is the addition of potassium iodide with carbon disulphide.

HI *b.* Forms iodine and hydrobromic acid. In presence of potassium hydrate forms potassium iodate and bromide.

$HCyS$ *c.* Forms hydrocyanic, hydrobromic, and sulphuric acids.

H_4FeCy_6 *d.* Forms hydroferricyanic and hydrobromic acids.

For classified statement of the action of chlorine, bromine, and iodine upon metallic forms, see 820 *h*, *i*.

Pb'' *f.* Forms PbO_2 and $Br^{-\prime}$ (a bromide). With fixed alkali only.

Hg' *g.* Forms Hg'' and a bromide, in alkaline and acid mixture.

Sn'' *h.* Forms Sn'''' and $Br^{-\prime}$ (a bromide). With fixed alkali and with acids.

Proof: After addition of potassium hydrate, potassium permanganate is not decolored.

Sb''' *i.* Forms Sb^{v} and $Br^{-\prime}$ (a bromide), with fixed alkali and with acids.

Proof same as above.

As''' *j.* Forms As^{v} and $Br^{-\prime}$ (a bromide).

Mn″ *k.* Forms MnO_2 and $Br^{-\prime}$ (a bromide), with fixed alkali. Not with acids.

Co *l.* Forms $Co_2(OH)_6$ and $Br^{-\prime}$ (a bromide), " "

Ni *m.* Forms $Ni_2(OH)_6$ and $Br^{-\prime}$ " "

Fe″ *n.* Forms $Fe^{\prime\prime\prime}$ and $Br^{-\prime}$ with fixed alkali and with acids.
In presence of fixed alkali, not with acids, it forms K_2FeO_4.

Cr‴ *o.* Forms Cr^{VI} and $Br^{-\prime}$, with fixed alkali and not with acids.

HYDROBROMIC ACID.

825. For general action see 820 *i.* and 532.

$HBrO_3$ *a.* Forms Br° and water, all the bromine being liberated from both acids.

HIO_3 *b.* Forms iodine and bromine.

PbO_2 *c.* Forms $PbBr_2$ and Br°.

Mn *d.* All compounds of manganese having more than two bonds are reduced to the dyad, and bromine is evolved.

$Co^{\prime\prime\prime}$ *e.* $Co^{\prime\prime\prime}$ and $Br^{-\prime}$ forms $Co^{\prime\prime}$ and Br°.

$Ni^{\prime\prime\prime}$ *f.* $Ni^{\prime\prime\prime}$ and $Br^{-\prime}$ forms $Ni^{\prime\prime}$ and Br°.

Cr^{VI} *g.* Cr^{VI} and $Br^{-\prime}$ forms $Cr^{\prime\prime\prime}$ and Br°.

BROMIC ACID.

826. Free bromic acid is so very instable that it is difficult to experiment with.

HI *a.* Forms free iodine and free bromine.

HCyS *b.* Forms **HCy**, H_2SO_4, **HBr**.

H_4FeCy_6 *c.* Forms hydroferricyanic and hydrobromic acids.

$Hg^{\prime}$ *d.* Forms $Hg^{\prime\prime}$ and $Br^{-\prime}$ (a bromide).

$Sn^{\prime\prime}$ *e.* Forms $Sn^{\prime\prime\prime\prime}$ and $Br^{-\prime}$. Proof: Does not decolor $KMnO_4$ after adding excess of **KHO**.

$Sb^{\prime\prime\prime}$ *f.* Forms Sb^{V} and $Br^{-\prime}$. " " "

$As^{\prime\prime\prime}$ *g.* Forms As^{V} and $Br^{-\prime}$. " " "

$Fe^{\prime\prime}$ *h.* Forms $Fe^{\prime\prime\prime}$ and $Br^{-\prime}$.

IODINE.

827. For the action of iodine upon the substances which precede it in the list given in 806, see the preceding paragraphs.

H_4FeCy_6 *a.* Iodine is decolored by potassium ferrocyanide, and some potassium ferricyanide and potassium iodide are formed. The action is slow, and never complete [*Gmelin's Hand-book*, 7, 459].

Hg' *b.* Forms Hg'' and I^{-1} with fixed alkali or with acids.

Sn'' *c.* Forms Sn'''' and I^{-1} " " "

Sb''' *d.* Forms Sb^{V} and I^{-1} [*Mohr, Titrirmethode*, 1870, 276].

As''' *e.* In alkaline mixture gives I^{-1} and As^{V}.

Mn'' *f.* Forms MnO_2 and I^{-1}, with fixed alkali, not with acids.

Co'' *g.* Forms Co_2O_3 and I^{-1} " " "

Fe'' *h.* Forms Fe''' and I^{-1} " " "

Cr''' *i.* Forms Cr^{VI} and I^{-1} " " "

Ni'' *j.* The bonds of Ni'' are not changed by iodine.

HYDRIODIC ACID.

828. See 820 *i*.

HIO_3 *a.* Liberates all the iodine from both acids.

H_4FeCy_6 *b.* Forms hydroferrocyanic acid and free iodine. The action is never quite complete.

Pb'''' *c.* Forms Pb'' and free iodine.

As^{V} *d.* Forms As''' and free iodine.

Sb^{V} *e.* Forms Sb''' and free iodine (423).

Cu'' *f.* Forms Cu' and free iodine (270).

Mn *g.* All compounds of manganese having more than two bonds are reduced to the dyad. If dilute hydriodic acid with $KMnO_4$ is used, manganese peroxide is first formed, and if the permanganate is in great excess potassium iodate is formed [*G. M. Donald, Amer. Jour. Pharmacy* (3), 17, 393].

Co''' *h.* Forms Co'' and free iodine.

Ni''' *i.* Forms Ni'' and free iodine.

Fe''' *j.* Forms Fe'' and free iodine.

Cr^{VI} *k.* Forms Cr''' and free iodine.

IODIC ACID.

829. The action of iodic acid upon the other acids has already been given.

$HCyS$ *a.* Forms hydrocyanic and sulphuric acids and free iodine.

H_4FeCy_6 *b.* Forms hydroferricyanic acid and free iodine.

Sn'' *c.* Forms Sn'''' and an iodide.

Proof: After addition of potassic hydrate does not decolor potassium permanganate.

Sb''' *d.* Forms Sb^{V} and free iodine. Proof as above.

As''' *e.* Forms As^{V} and free iodine. Proof as above.

Fe'' *f.* Forms Fe''' and free iodine.

HYDROCYANIC ACID.

830. In dilute solutions hydrocyanic acid is not readily oxidized, although some of the stronger, concentrated oxidizing agents decompose it. The products formed have not been thoroughly investigated.

THIOCYANIC OR SULPHOCYANIC ACID.

831. For action of this upon other acids see 811 to 829. It is quite instable. On being liberated from its salts it is soon resolved into hydrocyanic and persulphocyanic ($H_2Cy_2S_3$) acids. $3HCyS = HCy + H_2Cy_2S_3$ [*Watts' Dictionary*, 4, 378].

PbO_2 *a.* Forms Pb'' and sulphuric acid. In acid mixture only [*E. A. Hadow, Jour. Chem. Society*, 11, 174].

H_3AsO_4 *b.* Forms As''' hydrocyanic and sulphuric acids.

MnO_2 *c.* Forms Mn'' and sulphuric acid. In acid mixture only.

Mn^{VII} *d.* Forms Mn'', and in acid mixture, hydrocyanic and sulphuric acids. In alkaline mixture, cyanic, $HCyO$, and sulphuric acids are produced [*Wurtz's Dictionnaire de Chimie*, 3, 95].

Co''' *e.* Forms Co'', hydrocyanic and sulphuric acids.

Ni''' *f.* Forms Ni'', hydrocyanic and sulphuric acids.

Cr^{VI} *g.* Forms Cr''', hydrocyanic and sulphuric acids.

HYDROFERROCYANIC ACID.

832. The action of this upon the other acids is given in 806.

PbO_2 *a.* With sulphuric acid forms Pb'' and hydroferricyanic acid.

Ag' *b.* With fixed alkali, forms potassium ferricyanide and metallic silver.

MnO_2 *c.* With phosphoric acid, gives Mn'' and hydroferricyanic acid.

Mn^{VII} *d.* Forms with potassium hydrate MnO_2 and potassium ferricyanide. With sulphuric acid, manganous sulphate and hydroferricyanic acid.

Co''' *e.* With phosphoric acid, forms Co'' and hydroferricyanic acid.

Ni''' *f.* With acetic acid, gives Ni'' and hydroferricyanic acid.

Cr^{VI} *g.* With phosphoric acid, gives Cr''' and hydroferricyanic acid [*Schönbein, Jour. für Prakt. Chemie*, 20, 145].

HYDROFERRICYANIC ACID.

833. For the action of this acid upon others, see those acids in preceding paragraphs.

Pb'' *a.* With potassium hydrate, forms PbO_2 and potassium ferrocyanide [*Watts' Dictionary*, 2, 248].

Sn'' *b.* With potassium hydrate, forms potassium stannate, K_2SnO_3, and potassium ferrocyanide [*Watts' Dictionary*, 2, 248].

Mn'' *c.* With potassium hydrate, forms MnO_2 and potassium ferrocyanide [*Boudault, Jour. für Prakt. Chemie*, 36, 23].

Cr''' *d.* Forms in alkaline mixture a chromate and a ferrocyanide [*Boudault, Jour. de Pharmacie* (3), 7, 437].

LEAD OXIDE.

834. The reducing action of Pb'' upon acids has already been given.

Sn'' *a.* In alkaline mixture becomes Sn'''', and metallic lead is formed.

Mn^{VII} *b.* Produces a black precipitate containing both lead and manganese.

LEAD PEROXIDE.

835. For action of peroxide of lead upon acids, see preceding paragraphs.

Hg′ *a.* In acid mixture, changing **Pb′′′′** to **Pb″**, and **Hg″** is formed.

Sn″ *b.* In acid mixture **Pb′′′′** becomes **Pb″**, and in alkaline it is reduced to metallic lead, **Sn′′′′** being formed.

As‴ *c.* In alkaline and acid mixture becomes As^{V} and **Pb″**.

Mn″ *d.* In alkaline mixture gives **Mn′′′′** and **Pb″**, which uniting with excess of peroxide forms $PbO_2 4MnO_2$ [*Gibbs and Parkman, Amer. Jour. of Science* (2), 39, 58].

In acid mixture forms permanganic acid.

Fe″ *e.* In acid mixture changes **Pb′′′′** to **Pb″**, and **Fe‴** is formed.

Cr‴ *f.* In alkaline and acid mixture, **Pb′′′′** becomes **Pb″**, and **Cr‴** becomes Cr^{VI}.

SILVER OXIDE AND SALTS.

836. For action of acids on silver salts see 813–835.

Hg′ *a.* Forms metallic silver in acid and alkaline mixture [*Gmelin-Kraut, Handbuch der Chemie,* 3, 127].

As‴ *b.* In alkaline mixture forms metallic silver, and an arsenate.

Sb‴ *c.* In alkaline mixture forms argentous oxide, Ag_4O, and Sb^{V} [*Bunsen*].

Cu′ *d.* Becomes **Cu″**, and metallic silver is formed [*H. Rose, Jour. für Prakt. Chemie,* 71, 407].

Mn″ *e.* In neutral and ammoniacal mixture forms Ag_4O and Mn_2O_3 [*H. Rose, Jahresberichte für Chemie,* 1857, 252].

Co″ *f.* Forms in neutral and ammoniacal mixture Ag_4O and Co_2O_3 [*H. Rose, Chemical Gazette,* 15, 365].

Fe″ *g.* In slightly acid solution, metallic silver is formed and **Fe‴**. In ammoniacal mixture Ag_4O [*H. Rose, Jahresberichte für Chemie,* 1857, 252].

Cr‴ *h.* With potassium hydrate, gives metallic silver and potassium chromate.

MERCUROUS OXIDE.

837. Precipitated mercury is a little lighter in color than mercurous oxide, but when mixed with it is very difficult to identify in the presence of water. The method usually given is to digest with hydrochloric acid, and rub with a glass rod. A very tedious and unsatisfactory method if another precipitate, and especially mercurous oxide, is mixed with it.

A very good method is to permit it to settle, and decant, until thoroughly washed, then place in an evaporating dish and dry at a low temperature. The mercury will immediately collect in visible globules.

Sn″ *a.* In presence of acids and alkalies gives metallic mercury and **Sn‴′**.

As‴ *b.* In alkaline mixture, gives metallic mercury and **As^{v}**.

Sb‴ *c.* In strong alkaline mixture, gives metallic mercury and **Sb^{v}**.

$KMnO_4$. *d.* In acid mixture, gives **Mn″** and **Hg″**.
In alkaline mixture, gives **Hg″**, and first a green manganate, **Mn^{vi}**, and finally **Mn″**.

Cr‴ *e.* In alkaline mixture gives metallic mercury and **Cr^{vi}**.

MERCURIC OXIDE.

838. For action of mercuricum upon other substances, see preceding paragraphs.

Sn″ *a.* In acid and alkaline mixture, first mercurous oxide, then metallic mercury and **Sn‴′**.

As‴ *b.* In alkaline mixture, gives first **Hg′**, then **Hg^{o}** and **As^{v}**.

Sb‴ *c.* In very strong alkaline mixture, gives first **Hg′**, then **Hg^{o}** and **Sb^{v}**.

Fe″ *d.* In alkaline mixture, gives **Hg′** and **Fe‴**.

Cr‴ *e.* In alkaline mixture, gives first **Hg′**, then **Hg^{o}** and a chromate.

STANNOUS OXIDE.

839. For reaction of stannous oxide with acids, see preceding paragraphs.

As‴ *a.* With strong hydrochloric acid, elemental arsenic and stannic chloride are formed.

As^{v} *b.* First **Sn‴′** and **As‴** is formed, then as above.

Bi‴ *c.* In alkaline mixture, gives **Sn‴′** and **BiO**.

Cu'' *d.* In acid mixture forms Cu', in alkaline metallic copper and Sn'''' [*E. Lenssen, Jour. für Prakt. Chemie*, 79, 90].

Cd *e.* In alkaline mixture, gives metallic cadmium and Sn''''.

Mn^{VII} *f.* In acid and alkaline mixture, gives Sn'''', and Mn''.

Fe''' *g.* In acid mixture, changes Fe''' to Fe'', and Sn'''' is formed.

Cr^{VI} *h.* In acid and alkaline mixture, gives Sn'''' and Cr'''.

840. Stannic Compounds. See 813, 814, 820, 822, 823, 827, etc.

841. Antimonious Compounds. See 814, 820, 824, etc.

Mn *a.* In acid mixture, all compounds of manganese having more than two bonds are changed to the dyad, Sb^{V} being formed. In alkaline mixture the result is the same, except that a residue remains, probably Mn_3O_4.

Ni''' *b.* In alkaline mixture becomes Ni''.

Cr^{VI} *c.* In alkaline and acid mixture, gives Cr''' and Sb^{V}.

842. Antimonic Compounds. See 814, 820, 824.

843. Arsenious Compounds. See 814, 815, 820, 824, 827, etc.

Cu'' *a.* In alkaline mixture, As''' becomes As^{V}, and Cu' is formed.

Mn^{VII} and Mn'''' *b.* In acid mixture both are changed to Mn'', As^{V} being formed. In presence of alkalies a precipitate remains, which is perhaps manganese arsenate.

Co_2O_3 *c.* In acid mixture, gives As^{V} and Co''.

Ni_2O_3 *d.* In acid and alkaline mixture, gives As^{V} and Ni''.

Cr^{VI} *e.* In acid and alkaline mixture As''' becomes As^{V}, and Cr''' is formed.

843½. Arsenious Hydride.

HNO_2. Forms arsenious and arsenic oxides and nitric oxide.*

HNO_3. Forms arsenious and arsenic oxides and nitric oxide.†

H_2SO_3. Forms elemental arsenic, and probably a "lower sulphide" of arsenic.*

* H. B. Parsons, *Chemical News*, 35, 235.

† Gmelin's *Hand-book of Chemistry*, 4, 262.

H_2SO_4. Forms elemental arsenic and sulphurous anhydride.†

Later arsenious oxide and hydrosulphuric acid.‡

Cl Arsenious and arsenic oxides and hydrochloric acid.†

Br Arsenious and arsenic oxides and hydrobromic acid.†

I Arsenious oxide and hydriodic acid.†

HIO_3 Arsenious oxide and iodine.*

$HMnO_4$ In neutral solution, arsenic and manganic oxides. In acid solution, arsenious and arsenic oxides and manganous salt. In alkaline solution, arsenious and arsenic oxides, and manganic oxide.*

$HCrO_4$ In alkaline solutions, elemental arsenic and chromic oxide.*

844. Arsenic Compounds. See 811, 815, 817, 828, 831.

845. Bismuth Compounds. For the reactions of bismuth, see 820 and 839.

846. Copper Compounds.§

Cr''' *a.* In alkaline mixture Cu_2O is precipitated, and a chromate is formed.

Fe'' *b.* In acid mixture, Cu' and Fe''' are formed; in alkaline, metallic copper separates.

847. Manganous Compounds. See 820, 824, 827, etc.

848. Manganese Peroxide. See 815, 817, 818, 821, 825, 828, 831, etc.

849. Permanganates.§

Co'' *c.* In alkaline mixture MnO_2 and Co_2O_3 are formed.

Ni'' *d.* In alkaline mixture MnO_2 and Ni_2O_3 are formed.

Fe'' *e.* In acid mixture gives Mn'' and Fe'''.

850. Cobaltous Compounds. See 820, 824, 827, etc.

851. Cobaltic Compounds. See 811, 815, 817, 818, 821, 825, 828.

852. Nickelous Compounds. See 820, 824, etc.

853. Nickelic Oxide. See 811, 815, 817, 818, 821, 825, 828.

* H. B. Parsons, *Chemical News*, 35, 235.
† Gmelin's *Hand-book of Chemistry*, 4, 262.
‡ Watts' *Dictionary, Supplement*, 1, 218.
§ For other reactions of these substances, see preceding paragraphs.

854. Ferrous Compounds. See 813, 814, 820, 823.

855. Ferric Compounds. See 815, 817, 818, 828, 839.

856. Chromic Compounds. See 820, 824, 827, 835.

857. Chromic Acid. See 811, 813, 815, 817, 818, 825, 828, 831.

PRECIPITATION OF METALS BY METALS.

858. Metals frequently precipitate other metals from their solutions. Thus, in this list **Au, Pt, Ag, Hg, Cu** (**Pb** and **Sn**), **Co, Cd**, each metal precipitates all those which precede it, and is precipitated by all those which follow. Lead and tin precipitate all those which precede, and are precipitated by all those which follow; neither precipitates the other completely. Further, all in the list are precipitated by **Zn, Mg, Al, K**, and **Na**. Iron precipitates copper, and those which precede, but is only partially precipitated by those which follow, owing to its tendency, when in a finely divided state, to take up oxygen.

859. Nascent hydrogen, produced by action of acids upon metals, by action of water upon sodium amalgam, or by potassium or sodium hydrate upon metallic aluminium, reduces many acids. For example: Iodic becomes hydriodic or an iodide, in acid and in alkaline mixture. In the same way bromic and chloric acids are reduced to bromides and chlorides, and hydroferricyanic to hydroferrocyanic. In acid mixture, thiocyanic and sulphurous acids are reduced to hydrosulphuric, and hypophosphorus to PH_3.

EQUATIONS.

860. It is recommended that the student write all the equations representing the reactions given in this part. Below are given a few examples, which he should balance according to the principles given previously, using rule given in 810. It will be seen that in many cases an oxidizing agent is made to act upon two reducing agents, both in the same salt. Thus, in the 4th, the ferrosum and the hypophosphorous acid are both oxidized, and in the 8th both the mercurosum and the arsenious acids are oxidized, while in the 15th both the copper and arsenic are reduced.

It is to be understood that the right-hand ingredients are to be used in excess, or in as great quantities as may be necessary to fully oxidize or reduce the first ingredients. It is also recommended that the teacher extend this list to several hundred for class use.

1. $Pb_3O_4 + Mn_3(PO_4)_2 + HNO_3$
2. $FeI_2 + HNO_3$
3. $BaH_4(PO_2)_2 + KNO_3 + H_2SO_4$
4. $FeH_4(PO_2)_2 + HNO_3$
5. $Pb_3(AsO_3)_2 + KOH + Cl$
6. $Pb_3(AsO_3)_2 + Cl + H_2O + HCl$

7. $Hg_6(AsO_3)_2 + KOH + Cl$
8. $Hg_6(AsO_3)_2 + Cl + H_2O + HCl$
9. $Cr_2(NO_3)_6 + PbO_2 + KOH$
10. $FeSO_3 + KOH + Cl$
11. $PbI_2 + KOH + Cl$
12. $Mn_3(AsO_3)_2 + KOH + Cl$
13. $NiH_4(PO_2)_2 + KOH + Cl$
14. $HgSO_3 + Zn + HCl$
15. $Cu_3(AsO_4)_2 + HI$
16. $Bi(CyS)_3 + Al + HCl$
17. $Fe_2(AsO_4)_2 + HCl + H_2S$
18. $PbSO_3 + H_2O + Cl$
19. $Hg_2C_2O_4 + KOH + Cl$
20. $SnS + H_2O + Cl$
21. $CdSO_3 + Zn + HCl$
22. $MnSO_3 + H_2O + Cl$
23. $MnSO_3 + KOH + Cl$
24. $Cr_2(SO_3)_3 + KOH + Br$
25. $Cr_2H_{12}(PO_2)_6 + Cl + H_2O$
26. $Cr_2H_{12}(PO_2)_6 + KOH + Cl$
27. $Cr_2I_6 + KOH + Cl$
28. $Cr_2I_6 + KOH + Br$
29. $Pb(CyS)_2 + KOH + Cl$
30. $Pb(CyS)_2 + H_2O + Cl$
31. $Ba(CyS)_2 + Cl + H_2O$
32. $ZnI_2 + KOH + Br$
33. $ZnI_2 + KOH + Cl$
34. $FeI_2 + KOH + Cl$
35. $FeI_2 + KOH + I$
36. $Pb_3(AsO_4)_2 + C +$ fusion
37. $Al_2I_6 + Al_2(IO_3)_6 + H_3PO_4$
38. $K_2Cr_2O_7 + KNO_2 + H_3PO_4$
39. $SrSO_3 + H_2O + Cl$
40. $Sr(CyS)_2 + H_2O + Cl$
41. $K_2FeO_4 + Zn + H_3PO_4$
42. $Hg_3(AsO_4)_2 + H_3PO_2$
43. $Fe_2(AsO_4)_2 + H_3PO_2$
44. $Ni_2(OH)_6 + Zn + H_2SO_4$
45. $MnO_2 + Al + H_2SO_4$
46. $Fe_2(AsO_4)_2 + K_2S + HCl$
47. $Fe_2(AsO_4)_2 + Al + HCl$
48. $FeSO_3 + Al + HCl$
49. $K_2SnO_2 + BiCl_3 + KOH$
50. $Cu_3(AsO_4)_2 + HI$
51. $Hg_6(AsO_3)_2 + KOH + Br$
52. $Cu(IO_3)_2 + HI$
53. $PbCrO_4 + HI$
54. $Cu(NO_3)_2 + BaI_2 + H_2SO_4$
55. $AgMnO_4 + H_2S$
56. $PbH_4(PO_2)_2 + Zn + H_2SO_4$

PROBLEMS IN SYNTHESIS.

861. For the sake of more thorough drill in the principles of oxidation, a few problems are here given; a part of them the student should practically work at his table, but they are chiefly designed for class exercises. Special care should be taken that a pure product be formed, and that the ingredients be taken from the sources indicated. Thus, in the 31st, the chlorine for the ammonium chloride must be obtained from silver chloride, and the nitrogen of potassium nitrate must be converted into ammonia, and then united with the chlorine, and the product purified.

The student is not to suppose that these problems represent operations that are financially profitable, but merely chemical possibilities, and their solution will compel an accurate comprehension of a great variety of important principles. It is recommended that the teacher increase the number of these; an ordinary class may with profit discuss from three to five hundred.

1. Make pure mercuric bromide, from mercurous chloride and aluminic bromide.
2. " chromic chloride, " potassium chromate " hydrochloric acid.
3. " arsenic acid, " potassium arsenite.
4. " potassium arsenate, " potassium arsenite " potassium hydrate.
5. " plumbic nitrate, " plumbic chloride " zinc nitrate.
6. " mercurous nitrate, " mercuric chloride " bismuth nitrate.
7. " mercurous oxide, " mercuric oxide.
8. " mercuric bromide, " metallic mercury " potassium bromide.
9. " mercuric bromide, " metallic mercury " silver bromide.
10. " lead nitrate, " lead dioxide " potassium nitrate.
11. " mercurous phosphate, " phosphoric acid " mercuric chloride.
12. " barium sulphate, " lead sulphide " barium hydrate.
13. " bar'm hypophosphite, " calc'm hypophosphite " barium chloride.
14. " lead chromate, " chromic chloride " lead sulphate.
15. " chromic chloride, " potas. acid chromate " silver chloride.
16. " barium chromate, " chromic chloride " barium sulphate.
17. " mercuric chromate, " mercuric sulphide " chromium nitrate.
18. " chromium sulphate, " potas. acid chromate " bismuth sulphite.
19. " phosphoric acid, " sodium phosphate.
20. " phosphorus, " calcium phosphate.
21. " lead iodate, " lead sulphate " potassium iodide.
22. " silver iodate, " silver bromide " potassium iodide.
23. " ferric arsenate, " ferrous sulphide " arsenious acid.
24. " mercuric bromide, " mercuric sulphide " lead bromide,
25. " ammonium sulphate, " potassium nitrate " sulphur.
26. " ammonium chloride, " lead nitrate " silver chloride.
27. " sodium chloride, " sodium sulphate " silver chloride.
28. " phosphorus, " sodium phosphate.
29. " lead sulphide, " triplumbic tetroxide " bismuth thiocyanate.
30. " ferrous sulphite, " ferrous chloride " barium sulphate.
31. " ammonium chloride, " potassium nitrate " silver chloride.
32. " mercurous nitrate, " mercuric chloride " potassium nitrate.

33. Make pure potassium sulphate, from sodium sulphite and potassium nitrate.
34. " mercurous chloride, " mercurous sulphide " ferric chlorate.
35. " potassium iodide, " potassium chloride " sodium iodate.
36. " sodium iodate, " sodium chloride " potassium iodide.
37. " sodium phosphate, " potassium phosphate " sodium chloride.
38. " potassium bromide, " silver bromide " potassium chloride.
39. " potassium chloride, " silver chloride " potassium bromide.
40. " strontium nitrate, " strontium sulphate " mercurous nitrate.
41. " mercurous sulphide, " mercuric bromide " potassium sulphite.
42. " potassium sulphate, " sodium sulphate " potassium hydrate.
43. " sodium sulphate, " potassium sulphate " sodium hydrate.
44. " potassium chromate, " chromic chloride " potassium hydrate.
45. " potassium iodide, " sodium iodate " potassium nitrate.
46. " sodium iodate, " potassium iodide " sodium nitrate.
47. " potassium chloride, " sodium chloride " potassium nitrate.
48. " potassium carbonate, " oxalic acid " potassium chloride.
49. " ammonium sulphate, " potassium nitrate " sodium sulphide.
50. " manganese peroxide, " lead permanganate.
51. " arsenious sulphide, " lead arsenate " potas'm thiocyanate.
52. " arsenious sulphide, " lead arsenate " potassium sulphite.
53. " arsenious sulphide, " silver arsenate " barium sulphate.
54. " potassium nitrite, " sodium nitrite " potassium chloride.
55. " lead ferrocyanide, " cupric ferrocyanide " metallic lead.
56. " arsenic acid, " arsenious sulphide.
57. " lead sulphide, " lead sulphate.
58. " silver iodate, " silver iodide.
59. " stannous chloride, " stannic bromide and silver chloride.
60. " sodium sulphite, " sodium sulphate.
61. " sodium iodide, " sodium iodate.
62. " lead sulphide, " lead sulphite.
63. " lead sulphite, " lead sulphide.
64. " sulphuric acid, " arsenious sulphide.
65. " cadmium sulphite, " cadmium sulphate.
66. " ferrous sulphide, " ferric sulphate.
67. " cadm'm ferrocyanide, " cadmium ferricyanide.
68. " stannous chloride, " stannic sulphide and mercuric chloride.

69.	Make pure ferric bromide,	from	ferrous sulphide	and	silver bromide.
70.	" mercuric bromide,	"	mercurous chloride	"	silver bromide.
71.	" mercurous sulphide,	"	zinc thiocyanate	"	metallic mercury.
72.	" ammonium chloride,	"	silver nitrate	"	mercurous chloride.
73.	" barium carbonate,	"	calcium oxalate	"	barium chloride.
74.	" sodium hydrate,	"	sodium aluminate.		
75.	" potassium hydrate	"	potassium stannate.		

862. A few general principles are here given to aid the student in solving the preceding problems.

For the sake of brevity, the term *all salts* is frequently used, and it is to be understood that this does not include those of the rarer metals, but merely those of **Pb, Ag, Hg′, Hg″, Sn″, Bi, Cu″, Cd, Zn, Al, Co″, Ni, Mn″, Fe″, Fe‴, Cr‴, Ba, Sr, Ca, Mg, Na,** and **K.** It must be borne in mind that the methods given are not always the best, but those only are chosen which involve principles of universal application. Should one desire in each case to learn the most economical method, in all its details, used by the manufacturer, he is referred to the works upon chemical technology.

OXALATES.

863. *a.* Oxalates are formed by treating the oxide, hydrate, or carbonate with oxalic acid. In this manner may be made all oxalates (862).

b. By adding oxalic acid to some soluble salt of the metal. In this manner all oxalates (862) may be made except alkali, magnesium, chromic, ferric, aluminic, and stannic oxalates, which are not precipitated. Antimonious salts are precipitated, but the precipitate is basic.

c. Alkaline oxalates will precipitate the same solutions as oxalic acid, but many of the precipitates are soluble in excess of the alkaline oxalate, and, as a rule, the salt found is a double one, *e.g.*, $AgNH_4C_2O_4$. The fourth group metals are well-defined exceptions to this rule—their precipitates, formed by this method, being normal oxalates.

d. Some of the metals when finally divided are attacked by oxalic acid, hydrogen being evolved.

CARBONATES.

864. All the metals, in list 862, can be converted into carbonates, except antimony, tin, aluminium, chromium, and ferricum.

a. The alkaline carbonates precipitate solutions of all other metals, the precipitate with antimony salts is an oxide. With tin, aluminium, chromium, and

ferricum it is a hydrate; with silver salts, mercurous, cadmium, manganese, ferrous, and salts of the fourth group metals, it is a normal carbonate. In other cases the precipitate is a basic carbonate.

b. The above carbonates may also be made by passing carbonic anhydride into the moist hydrate. Dry carbonic anhydride in no case combines with dry oxides.

NITRITES.

865. The nitrites are all soluble; the silver and lead salts sparingly.

Nitrite of potassium may be made by fusion from the nitrate, oxygen being evolved, or by passing peroxide of nitrogen, N_2O_4, into potassium hydrate. Silver nitrite can be made from this by precipitation, and purified by recrystallization.

Basic lead nitrite can be made by boiling lead nitrate with metallic lead. The other nitrites are made by transposition; adding to silver nitrite, the chloride of the metal, which we wish to change to a nitrite, care being taken to add just enough. The nitrites of mercurosum, tin, antimony, bismuth, aluminium, iron, and chromium have not been made.

NITRATES.

866. Nitrates are all soluble. *a.* They are formed by the action of nitric acid upon metals, as described in 814. *b.* By dissolving the oxides, hydrates, or carbonates of the metals in nitric acid. Mercurous, stannous, manganous, and ferrous nitrates should not be evaporated to expel excess of nitric acid, since a higher metallic form would result. The crystals may be washed in cold water, to free them from the uncombined acid. All nitrates are decomposed by heat; a few, the alkalies and alkaline earths, first evolve oxygen and form nitrites, afterward a mixture of oxygen and nitrogen, leaving the oxides; others, either free nitric acid or a mixture of the oxides of nitrogen, until only the oxide of the metal remains. There are two exceptions, silver and mercury, in which cases only the free metals remain.

867. HYPOPHOSPHITES.

a. The hypophosphites are prepared by neutralizing the acid with bases; *b,* by double decomposition, adding the sulphates to barium hypophosphite. All the metals (862) form hypophosphites except mercurosum, copper, and tin. The silver and ferric salts are not very stable.

PHOSPHATES.

868. Phosphates can be made by adding phosphoric acid to the oxides, hydrates, or carbonates of the metals; but by this method it is usually diffi-

cult to add just a sufficient amount to make the normal salts. It is better to make them by precipitation. The normal silver, mercurous, bismuth, cadmium, zinc, manganous, cobaltous, nickel, and chromic phosphates are made by adding disodic hydric phosphate to solutions of the respective metals. A part of the acid with which the metal was combined is set free. Cupric and ferrous phosphates require the metallic solution to be added to the disodic hydric phosphate. (The reverse process gives some dimetallic phosphates.) Lead, aluminium, and ferric salts must be made from the acetates; mercuric from the nitrate (not chloride). The stannous salt made by precipitation from chloride contains stannous chloride, and the antimony salt is very basic. Disodic hydric phosphate throws down the alkaline earth metals, as dimetallic. To make the normal salts the trimetallic sodium phosphate should be used. The dimetallic phosphates of barium, strontium, and calcium may be made normal by addition of ammonium hydrate, but the magnesium salt, by this treatment, becomes $MgNH_4PO_4$. The phosphates are all soluble in phosphoric acid except the lead, mercurous, and bismuth salts.

SULPHIDES.

869. The sulphides of the first three groups, as also the method of making them, are too familiar to require description. The sulphides of the alkaline earths are usually made from the sulphates by fusion with charcoal. They are partially decomposed by water.

SULPHITES.

870. The sulphites are usually made by action of sulphurous acid upon the oxides or hydrates of the metals. They are normal, except mercurous, which is acid, and chromium, aluminium, and copper, which are basic. Sulphurous acid precipitates solutions of metals of the first and second groups, except copper and cadmium.

The sulphites of the alkalies precipitate solutions of the other metals except chromium salts; and some normal sulphites may be made in this manner. The sulphites of silver, mercury, copper, and ferricum (known only in solution) are instable, the sulphurous acid becoming sulphuric at the expense of the base, which is reduced to a form having a less number of bonds. With the instable stannous sulphite the action is the reverse. (See 818.) All sulphites by exposure to the air slowly absorb oxygen, and are partially converted into sulphates.

SULPHATES.

871. Sulphates are made, *a*, by dissolving the metals in sulphuric acid, 819; *b*, by dissolving the oxides or hydrates; *c*, by displacement. All salts

containing volatile acids are displaced by sulphuric acid and a sulphate formed (except the chlorides of silver, mercury, and tin). The excess of acid may generally be expelled by evaporation, or the crystals washed with cold water or alcohol.

The insoluble sulphates are best made by precipitation.

CHLORIDES.

872. Chlorides may be made, *a*, by direct union of the elements, mostly without heat. Whether an *ous* or *ic* salt is formed depends upon the amount of chlorine used. *b*. By the action of hydrochloric acid upon the corresponding oxides, hydrates, carbonates, or sulphites, with the exception of antimony and bismuth salts, which become basic. The solutions formed may be evaporated to expel excess of acid. If the chlorides thus formed contain water of crystallization it cannot be removed by heat alone, for part of the acid is by this means driven off, and a basic salt remains. If the anhydrous chloride is desired, it may always be made by *a*, and when thus formed may be sublimed without decomposition. *c*. Chlorides of the first group are best made by precipitation. Exception: *Mercuric* chloride does not precipitate *lead* salts. *d*. Metals soluble in hydrochloric acid evolve hydrogen and form chlorides. In these cases *ous*, and not *ic*, salts are formed.

CHLORATES.

873. Chlorates may be made by action of chloric acid upon the oxides, hydrates, or carbonates of the metals, or by adding barium chlorate in molecular proportions to soluble sulphates. By these methods all (862) the normal chlorates may be made. The mercurous and ferrous salts are very instable, and those of antimony, tin, bismuth, and manganese are not with certainty known.

BROMIDES.

874. *Metallic bromides* may be made, *a*, like chlorides, 872, *a*, but the action is less rapid, and in some cases heat is required; *b*, like chlorides, 872, *b*, with the same precautions throughout; *c*, first group metals are best made by precipitation. Mercuric bromide may be precipitated from mercuric nitrate, but not from mercuric chloride. And, *d*, like chlorides, 872, *d*, but fewer bromides can be made by this method.

IODIDES.

875. Metallic iodides may be made, *a*, like chlorides, 872, *a*. Iodine unites less readily with metals than chlorine or bromine, but by the aid of heat they may all be formed if the metal is finely divided.

b. Like chlorides, 872, *b.* *c.* Iodides of the first group, and cuprosum, are best made by precipitation. *d.* Like 860, *d*, except that many of the heavy metals are insoluble in hydriodic acid.

Cupric iodide is not known. Ferric iodide is known only in solution.

IODATES.

876. Iodates are made by action of iodic acid on the oxides, hydrates, or carbonates of the metals. In this manner are made the normal iodates of lead, silver, mercury, bismuth, copper, cadmium, zinc, cobalt, nickel, manganese, barium, strontium, and calcium. Other iodates may be thus made, but their precise composition is not determined.

APPENDIX.

SOLUBILITIES OF METALLIC SALTS.

I. THE SALTS OF EACH BASE.

	Soluble in water.	*Insoluble in water.*
Aluminium	Acetate. Bromide. Chlorate. Chloride. Iodate. Iodide (instable). Nitrate. Nitrite. Silicofluoride. Sulphate. Sulphite. Sulphocyanate. Tartrate.	Antimoniate. Arseniate. Borate (instable). Hydrate. Oxalate (sparingly soluble). Phosphate.
Ammonium	*All except those named in the other column.*	Phosphomolybdate. Platinic Chloride (very sparingly soluble). Acid Tartrate (sparingly soluble). Nitrophenate (sparingly soluble).
Antimonious	Acetate. Fluoride. Tartrate.	Arseniate. Chromate. Oxalate (sparingly soluble). Oxide. Phosphate. Sulphide. Sulphite. Tannate, } Soluble in dilute acid. Bromide, } Chloride, } Iodide, } Sulphate, }

	Soluble in water.	*Insoluble in water.*
Arsenious	Oxide (sparingly).	Bromide, Chloride, Iodide, Sulphide. } Decomposed.
Barium	Acetate. Bromide. Chlorate. Chloride. Citrate. Cyanate. Ferricyanide (sparingly). Ferrocyanide. Hydrate paringly). Iodide. Nitrate. Sulpharsenite. Sulphides. Sulphocyanate. Thiosulphate (sparingly).	Carbonate. Chromate. Cyanide (sparingly soluble). Iodate. Manganate. Molybdate. Oxalate. Phosphate. Silicofluoride. Sulphate. Sulphite. Tartrate.
Bismuth	Acetate. Bromide, Chlorate, Chloride, Nitrate, Sulphate, } Soluble in acidulated, decomposed by pure water.	Arseniate. Borate. Carbonate (basic). Chromate. Citrate. Ferrocyanide. Hydrate. Iodate. Iodide (decomposed). (Basic) Nitrate. Oxalate. Phosphate. Sulphide. Tartrate. Tannate.
Cadmium	Acetate. Bromide. Chloride. Iodide. Nitrate. Sulphate.	Borate (sparingly soluble). Carbonate. Chromate. Citrate (sparingly soluble) Hydrate. Oxalate. Phosphate. Sulphide. Tartrate.

	Soluble in water.	*Insoluble in water.*
Calcium	Bromide.	Antimoniate.
	Chlorate.	Arseniate.
	Chloride.	Arsenite.
	Chromate.	Borate (sparingly soluble).
	Cyanide.	Carbonate.
	Ferricyanide.	Citrate.
	Ferrocyanide.	Ferrocyanide (Potassio).
	Hydrate (sparingly).	Iodate (sparingly soluble).
	Hypophosphite.	Molybdate.
	Iodide.	Oxalate.
	Nitrate.	Phosphate.
	Sulpharsenite.	Sulphate (sparingly soluble).
	Sulphides.	Tartrate (sparingly soluble).
	Sulphocyanate.	
	Thiosulphate.	
Cerium	Acetate.	Carbonate.
	Chloride.	Ferrocyanide.
	Sulphate (hydrated).	Hydrate.
		Oxalate.
		Phosphate.
		Sulphate (anhydrous).
		Sulphate (Potassio).
Chromium	Acetate.	Arseniate.
	Bromide.	Hydrate.
	Chloride.	Phosphate.
	Iodide.	
	Nitrate.	
	Oxalate.	
	Sulphate.	
	Sulphite.	
Cobalt	Acetate.	Antimoniate.
	Bromide.	Arseniate.
	Chloride.	Arsenite.
	Iodide.	Borate.
	Nitrate.	Carbonate (basic).
	Sulphate.	Chromate (basic).
	Sulphocyanate.	Cyanide.
	Tartrate.	Ferricyanide.
		Ferrocyanide.
		Hydrate.
		Oxalate.
		Phosphate.
		Sulphide.
Copper	Acetate.	Antimoniate.
	Chlorate.	Arseniate.
	Chloride.	Arsenite.

	Soluble in water.	*Insoluble in water.*
Copper	Nitrate.	Borate.
	Permanganate.	Carbonate (basic).
	Sulphate.	Chromate (basic).
	Sulphocyanate.	Citrate (sparingly soluble).
		Cyanide.
		Ferricyanide.
		Ferrocyanide.
		Hydrate.
		Iodate.
		Iodide (decomposed).
		Iodide (cuprous).
		Oxalate.
		Phosphate.
		Sulphide.
		Sulphite (sparingly soluble).
Glucinium	Chloride.	Carbonates (basic).
	Sulphate.	Ferrocyanide.
		Hydrate.
		Phosphate.
Gold :		
Auric	Bromide.	Cyanide.
	Chloride.	Iodide (decomposed).
		Sulphide.
Iron :		
Ferrous	Acetate.	Antimoniate (slightly soluble).
	Bromate.	Arseniate.
	Bromide.	Arsenite.
	Chlorate.	Borate.
	Chloride.	Carbonate.
	Citrate.	Cyanide.
	Iodide.	Ferricyanide.
	Nitrate.	Ferrocyanide.
	Silicofluoride.	Hydrate.
	Sulphate.	Iodate (sparingly soluble).
	Sulphocyanate.	Molybdate.
	Thiosulphate.	Oxalate,
		Phosphate.
		Sulphide.
		Sulphite.
		Tannate.
		Tartrate (slightly soluble).
Ferric	Acetate.	Antimoniate.
	Bromate.	Arseniate.
	Bromide.	Arsenite.
	Chlorate.	Borate.
	Chloride.	Chromate (decomposed).
	Citrate.	Ferrocyanide.

	Soluble in Water.	*Insoluble in Water.*
Iron :		
Ferric	Ferricyanide.	Hydrate.
	Iodide.	Iodate (sparingly soluble).
	Nitrate.	Oxalate (slightly soluble).
	Silicofluoride.	Phosphate.
	Sulphate.	Sulphide.
	Sulphite (instable).	Tannate.
	Sulphocyanate.	
	Tartrate.	
Lead	Acetate.	Antimoniate.
	Acetate (basic).	Arseniate.
	Chlorate.	Arsenite.
	Nitrate.	Borate.
	Nitrite.	Bromate (sparingly soluble).
		Bromide (sparingly soluble).
		Carbonate (basic).
		Chloride (sparingly soluble).
		Chromate.
		Citrate.
		Cyanide.
		Ferricyanide.
		Ferrocyanide.
		Fluoride (sparingly soluble).
		Hydrate.
		Iodate.
		Iodide (sparingly soluble).
		Molybdate.
		Oxalate.
		Phosphate.
		Sulphate.
		Sulphide.
		Sulphite.
		Sulphocyanate (sparingly soluble).
		Tannate.
		Tartrate.
		Thiosulphate (sparingly soluble).
Lithium	Acetate.	Carbonate (sparingly soluble).
	Chlorate.	Phosphate.
	Chloride.	Silicofluoride (sparingly soluble).
	Chromate.	
	Citrate.	
	Hydrate.	
	Iodate.	
	Iodide.	
	Nitrate.	
	Oxalate.	
	Sulphate.	
	Sulphide.	
	Tartrate.	

	Soluble in Water.	*Insoluble in Water.*
Magnesium	Acetate. Bromide. Chlorate. Chloride. Chromate. Cyanide. Ferricyanide. Ferrocyanide. Iodate. Iodide. Molybdate. Nitrate. Nitrite. Permanganate. Sulphate. Sulphide. Sulphite (sparingly). Tartrate (sparingly). Thiosulphate.	Aluminiate. Antimoniate. Arseniate. Borate. Carbonate (basic). Hydrate. Oxalate (sparingly soluble). Phosphate.
Manganese	Acetate. Chlorate. Chloride. Chromate. Iodide. Nitrate. Sulphate. Sulphocyanate. Tartrate. Thiosulphate.	Antimoniate. Arseniate. Borate. Carbonate. Cyanide. Ferricyanide. Ferrocyanide. Hydrate. Oxalate. Phosphate. Sulphide. Sulphite.
Mercurous	Acetate (sparingly). Chlorate (sparingly). Nitrate. Sulphate (sparingly).	Borate. Bromide. Chloride. Chromate. Citrate. Ferricyanide. Ferrocyanide. Iodide. Oxalate. Oxide. Phosphate. Sulphide. Sulphocyanate.
Mercuric	Acetate. Bromide (sparingly). Chlorate.	Arseniate. Arsenite. Borate.

	Soluble in Water.	*Insoluble in Water.*
Mercuric		Carbonate (basic).
	Chloride.	Citrate.
	Chromate (sparingly).	Ferrocyanides (instable).
	Cyanide.	Iodide.
	Nitrate (in acidulated water).	Oxalate (sparingly soluble).
	Sulphate " "	Oxide.
	Sulphocyanate (sparingly).	Phosphate.
		Sulphide.
		Sulphite.
		Tartrate.
Nickel	Acetate.	Arseniate.
	Bromide.	Borate.
	Chloride.	Carbonate (basic).
	Chromate (acid salt).	Cyanide.
	Citrate.	Ferricyanide.
	Iodide.	Ferrocyanide.
	Nitrate.	Hydrate.
	Sulphate.	Oxalate.
		Phosphate.
		Sulphide.
Palladious	Bromide.	Cyanide.
	Chloride.	Iodide.
	Nitrate.	Oxide.
		Sulphate (decomposed).
		Sulphide.
Platinic	Bromide.	Iodide (soluble as acid salt).
	Cyanides (double).	Oxide.
	Nitrate.	Sulphide.
	Sulphate.	
Potassium		Nitrophenate (sparingly sol.)
	All except those named in the other column.	Perchlorate (sparingly sol.)
		Platinic chloride (sparingly sol.)
		Phosphomolybdate (sparingly sol.)
		Silicofluoride (sparingly sol.)
		Tartrate (acid), (sparingly sol.)
Silver	Acetate (sparingly).	*All except those in the other column.*
	Chlorate.	
	Fluoride.	
	Hypophosphite.	
	Lactate.	
	Nitrate.	
	Nitrite.	
	Permanganate (sparingly).	
	Sulphate (sparingly).	

	Soluble in Water.	*Insoluble in Water.*
Sodium		Antimoniate.
	All except those in the other column.	Silicofluoride (sparingly).
Strontium	Acetate.	Borate.
	Arsenite (sparingly).	Carbonate.
	Bromide.	Chromate (sparingly soluble).
	Chlorate.	Citrate.
	Chloride.	Hydrate (slightly soluble).
	Cyanide.	Molybdate.
	Ferricyanide.	Oxalate (sparingly soluble).
	Ferrocyanide.	Phosphate.
	Hypophosphite.	Sulphate (slightly soluble).
	Iodate (sparingly).	Tannate.
	Iodide.	Tartrate.
	Nitrate.	
	Nitrite.	
	Sulphocyanate.	
	Thiosulphate.	
Tin :		
Stannous	Acetate.	Arseniate.
	Bromide.	Borate.
	Iodide.	Ferrocyanide.
	Sulphate.	Hydrate.
	Tartrate (sparingly).	Iodate.
	Chloride, Nitrate, } in acidulated water.	Oxalate
		Phosphate.
		Sulphide.
Stannic	Acetate.	Chromate.
	Bromide.	Ferrocyanide.
	Chloride.	Hydrate.
	Nitrate (instable).	Iodide (instable).
	Oxalate.	Oxide.
	Sulphate.	Phosphate.
		Sulphide.
Uranous	Acetate.	Carbonate.
	Bromide.	Ferrocyanide.
	Chloride.	Hydrate.
	Iodide.	Oxalate.
	Nitrate.	Phosphate.
	Sulphate.	Sulphide.

	Soluble in Water.	*Insoluble in Water.*
Uranic	Acetate.	Carbonates (potassio, etc.)
	Bromide.	Ferrocyanide.
	Chloride.	Hydrate.
	Nitrate.	Oxalate.
	Sulphate.	Phosphate.
Zinc	Acetate.	Antimoniate.
	Bromide.	Arseniate.
	Chlorate.	Borate.
	Chloride.	Carbonate (basic).
	Chromate.	Cyanide.
	Iodide.	Ferricyanide.
	Nitrate.	Ferrocyanide.
	Permanganate.	Hydrate.
	Sulphate.	Iodate (sparingly soluble).
	Sulphite (sparingly).	Oxalate.
	Thiosulphate.	Phosphate.
		Sulphide.
		Tartrate.

II. SOLUBILITIES OF THE SALTS OF EACH ACID.

Concerning salts insoluble in water, it is stated by what *acids* they are **transposed**, and from this it will be seen by what acids they may be dissolved, *i.e.*, changed to compounds soluble in water. Concerning the transposition of salts soluble in water, see **19.** As to the solution of salts insoluble in water (and acids) by decomposition with *alkalies*, see 677. For more specific statements as to decomposing and dissolving agents, refer to the descriptions of the acids in question in the text.

Acetates. *All soluble in water;* Silver and Mercurous are sparingly soluble.

Arseniates. Closely resemble the (ortho)phosphates, both in solubilities and in transposition with acids.

Arsenites. *Those of the Alkali bases are soluble.* Those of Barium and Strontium, sparingly soluble ; the others are insoluble in water, but *transposed by dilute acids.*

Borates. *Only those of the Alkali bases are freely soluble in water;* many of the others being slightly soluble. They are *transposed by all acids, except carbonic.* Some of the metals form non-normal borates.

Bromates. *All soluble in water;* Silver, Lead, and Mercurous, sparingly soluble.

Bromides. Silver, Lead, and Mercurous, insoluble ; Mercuric, sparingly soluble ; Bismuth, instable ; *all others soluble in water.* The bromides insoluble in water are *scarcely transposed with sulphuric acid, or with dilute nitric acid* (533).

Carbonates. *Those of the Alkali bases only are soluble in water.* The acid carbonates less abundantly than the normal. Most of the others are made slightly soluble by free carbonic acid. Carbonates are *transposed by all acids*, except hydrosulphuric and hydrocyanic. The pseudo-triads do not form carbonates ; some other heavy metals form basic carbonates in the wet way.

Chlorates. *All soluble in water.* Potassium chlorate but moderately soluble.

Chlorides. Silver and Mercurous, insoluble ; Lead, slightly soluble ; *all others soluble in water ;* antimonious, stannous and bismuth, soluble in acidulated water.

Chromates. Those of the bases of the Alkalies, and Magnesium, Calcium, and Zinc, are soluble in water; Strontium and Mercuric, sparingly soluble; nearly all others insoluble. Iron, Manganese, and Copper form chromates not normal—some of which are soluble in water, but chiefly instable in solution.

Citrates. Those of the Alkali bases are freely soluble in water ; of Iron, Copper, and Zinc, moderately soluble ; *the other (single) citrates, mostly insoluble ;* the double citrates mostly soluble. The insoluble citrates are *transposed by dilute mineral acids.*

Cyanides. *Mostly insoluble in water ;* except those of the Alkali and Alkaline earth metals, and *double cyanides* containing these. Barium cyanide is sparingly soluble. Cyanides are *transposed by nearly all acids,* even when dilute.

Ferricyanides. Those of *the Alkali and Alkaline earth bases are soluble* in water ; that of Barium, sparingly. A considerable number of the others are insoluble in water, and certain of the bases do not form ferricyanides. See 632. They differ as to *transposition* with acids, but those insoluble are transposed by alkalies.

Ferrocyanides. Those of *the Alkali bases and* of Magnesium, Calcium (not the potassio calcium), and Strontium are soluble in water. See 629. Those insoluble differ as to transposition by acids, but are transposed by alkalies.

Fluorides. *Those of the Alkali bases* are freely soluble in water ; those of the Alkaline earth metals insoluble ; of Copper, Bismuth, Cadmium, Ferricum, and Zinc, sparingly soluble ; Silver, Tin, and Mercuric, soluble. The insoluble fluorides are *transposed* by strong sulphuric acid, and less easily by hydrochloric and nitric acids.

Hypochlorites. *All soluble in water.* (Decomposed by all acids.)

Hypophosphites. *All soluble in water.* (Decomposed by nearly all acids.)

Iodates. Only those of *the Alkali bases are freely soluble ;* the others insoluble, or sparingly soluble. Calcium, sparingly soluble ; Barium, Silver, and Lead, insoluble. *Transposed* by moderately dilute mineral acids—those of Silver and Lead by nitric acid not dilute.

Iodides. Silver, Lead, Mercurous, Mercuric (and Palladious), *insoluble* in water. Bismuth, and to some extent Copper iodides, are decomposed by water without solution. (295.) The others are soluble. The insoluble Iodides are *transposed* with difficulty, or not at all, by sulphuric acid or nitric acid. (556.)

Nitrates. *All soluble in water.*

Nitrites. *All soluble in water ;* Silver, sparingly.

Nitrophenates. *All soluble in water ;* Potassium, Ammonium, and Lithium, very sparingly ; most others, more freely.

Oxalates of the Alkali bases are soluble ; Chromium and Stannic oxalates, soluble ; Magnesium and Ferric oxalates, sparingly soluble ; the others chiefly insoluble or slightly soluble. *Transposed* by sulphuric, hydrochloric, and nitric acids, not by acetic.

Permanganates. *All soluble in water;* Silver, sparingly. A number of the bases decompose the acid radical.

Phosphates (ortho-). Of the di- and tri-metallic salts, *only those of the ordinary Alkali bases are soluble in water.* (Lithium, insoluble.) Those two-thirds hydric ("acid phosphates") are all soluble in water, to some extent. Acetic acid *transposes* most of the insoluble phosphates, except those of Iron, Aluminium, and Lead; and dilute hydrochloric, nitric, and sulphuric acids transpose all phosphates (partly or wholly, 707).

Pyrophosphates are *insoluble* in water, except those of the common Alkali bases. They are scarcely at all *transposed* by acetic acid, but yield their bases to the stronger acid radicals.

Metaphosphates of the common Alkali bases, only, are soluble in water. They are not *transposed* with acetic acid, and some of them not readily by other acids when dilute.

Silicates. *Those of the Fixed Alkali bases, only, are soluble* in water. These, in solution, are transposed by all acids. Of the silicates insoluble in water, many are *transposed* with hydrochloric or sulphuric acid, but the larger number of the natural silicates resist acids. All are decomposed by hydrofluoric acid, and by the fixed alkalies.

Sulphates. Those of Barium, Lead, Strontium, Calcium, are insoluble in water, the last-named being slightly soluble. (77.) Argentic and Mercurous sulphates are sparingly soluble. Mercuric, Antimonious, and Bismuth sulphates require acidulated water for solution. *All others are soluble in water.* Sulphates are not transposed with acids, at ordinary temperatures.

Sulphites. *Those of the Alkali bases are soluble—all others insoluble,* or very sparingly soluble in water. Those of the Alkaline earth metals are somewhat soluble in solution of sulphurous acid. All sulphites are *transposed* by acetic and the mineral acids.

Sulphides. Of the bases of the Alkalies and Alkaline earths, soluble; the others insoluble in water. The earth metals do not form sulphides. Sulphides of the third group metals are transposed with dilute acids; those of the second group metals (except Mercury), transposed or decomposed by hydrochloric, nitric and sulphuric acids.

Sulphocyanates. Those of Alkali and Alkaline earth bases, and of Iron, Manganese, Zinc, Cobalt, and Copper, are *soluble* in water. Mercuric, sparingly soluble. The others are *transposed* by dilute acids.

Tartrates. Those of the Alkali bases are soluble in water, the acid tartrates of Potassium, Ammonium, Rubidium, and Cæsium, but sparingly soluble. Manganous, Ferric, Cobalt, Stannous, and Antimonious tartrates are soluble; Calcium tartrate, slightly soluble. The other tartrates, not soluble in water, are mostly somewhat soluble in solution of tartaric acid, and mostly soluble in solutions of Alkalies (as double tartrates); also *transposed* by the mineral acids.

Thiosulphates. *All soluble in water;* those of Barium, Lead, and Silver, sparingly soluble in water, but made soluble as double salts. *Decomposed* by all acids, 697.

SOLUBILITIES OF METALLIC SALTS.

S, soluble in water. *s*, sparingly soluble in water. *i*, insoluble in water, but made soluble by acids. I, insoluble in water or acids.
s I, sparingly soluble in water, not transposed by acids. S *i*, soluble in acidulated water.

	Aluminium.	Ammonium.	Antimonious.	Barium.	Bismuth.	Cadmium.	Calcium.	Chromium.	Cobalt.	Copper.	Gold (triad).	Hydrogen.	Iron (dyad).	Iron (ps. triad).	Lead.	Magnesium.	Manganous.	Mercuric.	Mercurous.	Nickel.	Potassium.	Silver.	Sodium.	Stannic.	Stannous.	Strontium.	Zinc.
Acetate,	S	S	S	S	S	S	S	S	S	S		S	S	S	S	S	S	S	s	S	S	s	S	S	S	S	s
Arseniate,	s	s	s	s	s	s	s	s	s	s		S	S	S	s	s	s	s	s	S	S	s	S	s	s	s	s
Arsenite,	s	s	S	s	s	s	s	s	s	s		S	S	S	s	s	s	s	s	S	S	s	S	s	s	s	s
Borate,	s	s	s	s	s	s	s	s	s	s		S	S	S	s	s	s	s	s	S	S	s	S	s	s	s	s
Bromide,	S	S	S	S	Si	S	S	S	S	S	S	S	S	S	Is	S	S	S	s	S	S	I	S	S	S	S	S
Carbonate,	s	s	s	s	s	s	s	s	s	s		s	s	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Chlorate,	S	S	S	S	S	S	S	S	S	S		S	S	S	S	S	S	S	s	S	S	s	S	S	Si	S	S
Chloride,	S	S	Si	Si	Si	S	S	S	S	S	S	S	S	S	Is	S	S	S	s	S	S	I	S	S	S	S	S
Chromate,	s	s	s	s	s	s	s	s	s	s		S	s	s	s	s	s	s	s	s	S	s	S	s	s	s	s
Cyanide,		S								s		S	s		s	I	I	S	s	I	S	s	S	s	s	S	s
Ferricyanide,		S			I				I	I		S	I	S	s	I	I		s	I	S	s	S	s	s	S	s
Ferrocyanide,		S			s				s	s		S	s	s	s	s	s	S	s	s	S	s	S	s	s	S	s
Fluoride,	s	S	S	s	s	s	s	s	s	Si		S	s	s	s	s	s	s	s	s	S	s	S	Si	s	S	s
Hydrate,	s	S	Si	s	Si	s	s	s	s	s		S	S	S	s	s	s	s	s	S	S	s	S	Si	s	S	s
Iodide,	S	S	S	S	Si	S	S	S	S	S	S	S	S	S	S	S	S	S	s	S	S	I	S	S	Si	I	S
Nitrate,	s	S	s	s	s	s	s	s	s	s		S	s	s	s	s	s	s	s	s	S	s	S	s	s	s	s
Oxalate,	s	S	s	s	s	s	s	s	s	s		S	s	s	s	s	s	s	s	s	S	s	S	s	s	s	s
Oxide,	s	S	Si	I	Si	s	s	s	s	s		S	s	s	s	s	s	s	s	s	S	s	S	s	s	s	s
Phosphate,	s	S	Si	Si	Si	s	s	s	s	s		S	s	s	s	s	s	s	s	s	S	s	S	s	s	s	s
Sulphate,	S	S	S	S	S	S	S	S	S	S		S	S	S	S	S	S	S	s	S	S	s	S	S	S	S	S
Sulphide,	s	S	s	s	s	s	s	s	s	s		S	s	s	s	s	s	s	s	s	S	s	S	s	s	s	s

REAGENTS.*

[Aq. = H_2O as crystallization water.]

Acid, Acetic, $H(C_2H_3O_2)$. Sp. grav. 1.04. 30 p.c. acid.

Hydrochloric, HCl. Sp. grav. 1.12. 24 p.c. acid.

Hydrosulphuric, H_2S. Water saturated with the acid (663).

Hydrofluosilicic, $(HF)_2SiF_4$. (746.)

Nitric, HNO_3. Sp. grav. 1.2 (32 p.c. acid).

Nitro-hydrochloric, $NOCl_2 + Cl$. About one part of concentrated Nitric to 3 parts of Hydrochloric acid.

Nitrophenic, $HC_6H_2(NO_2)_3O$. (600.)

Oxalic, $H_2C_2O_4$. 2 aq. Crystals dissolved in 10 parts of water.

Sulphuric, H_2SO_4. Concentrated, sp. grav. 1.843.

Tartaric, $H_2(C_4H_4O_6)$. Crystals dissolved in 3 parts of water.

Chlorine Water, Cl. Water saturated with chlorine (501).

Alcohol, C_2H_6O. Sp. grav. .815. About 95 p.c.

Ammonium Chloride, NH_4Cl. One part crystallized salt in 8 parts of water.

Ammonium Carbonate, $(NH_4)_2CO_3$. One part of crystallized salt in 4 parts water, with one part of solution of Ammonia. As a solvent for arsenious sulphide, the reagent is prepared without the addition of solution of ammonia, $(NH_4)_4H_2(CO_3)_3$.

Ammonium Hydrate, NH_4OH. Sp. grav. .96. 10 p.c. NH_3.

Ammonium Molybdate, $(NH_4)_2MoO_4$. Solution in Nitric acid.

Ammonium Sulphide, $(NH_4)_2S$, colorless; $(NH_4)_2S_2$ or NH_4HS, yellow; solution of ammonia, treated with hydrosulphuric acid.

Ammonium Oxalate, $(NH_4)_2C_2O_4$. One part of the crystallized salt (aq.) in 24 parts of water.

Barium Chloride, $BaCl_2$. One part of the crystallized salt (2 aq.) to 10 parts of water.

Barium Carbonate, $BaCO_3$. (87).

Barium Hydrate, $Ba(OH)_2$. A saturated water solution (77).

Barium Nitrate, $Ba(NO_3)_2$. One part to 15 of water.

* In the greater number of cases, reagents should be "chemically pure." Different uses require different degrees of purity. An article of sodium hydrate contaminated with chloride, may be used in some operations; not in others. Those who have had training in analysis can do without specific directions, which cannot be made to cover all circumstances; and the beginner must depend on others for the selection of reagents.

Calcium Chloride, $CaCl_2$. One part salt (6 aq.) dissolved in 8 parts of water.

Calcium Hydrate, $Ca(OH)_2$. A saturated water solution (103), also the dry solid.

Calcium Sulphate, $CaSO_4$. A saturated water solution (77).

Carbon Disulphide, CS_2. (539.)

Cobaltous Nitrate, $Co(NO_3)_2$. One part crystallized salt (5 aq.) dissolved in 8 parts of water.

Copper Sulphate, $CuSO_4$. One part of the crystallized salt (5 aq.) in 8 parts of water.

Ether, $(C_2H_5)_2O$. Sp. grav. Not over .728—containing not over 5 p.c. alcohol.

Ferrous Sulphate, $FeSO_4$. One part crystallized (7 aq.) in 10 parts of water (169).

Ferric Chloride, Fe_2Cl_6. One part of the solid salt (6 aq.) to 15 parts of water.

Gold Chloride, $AuCl_3$. Prepared by dissolving pure gold—which may be obtained by precipitation with Oxalic acid—in nitro-hydrochloric acid, evaporating to dryness on the water-bath, and dissolving in water.

Lead Acetate, $Pb(C_2H_3O_2)_2$. One part of the crystallized salt (3 aq.) dissolved in 10 parts of water.

Magnesium Sulphate, $MgSO_4$. One part of the crystallized salt (7 aq.) to 10 parts of water.

Mercuric Chloride, $HgCl_2$. One part of the crystallized salt in 16 parts of water.

Mercurous Nitrate, $Hg_2(NO_3)_2$. One part of the crystallized salt (2 aq.) dissolved in 20 parts of water, acidulated with one part nitric acid, or prepared by dissolving mercury (343).

Palladious Chloride, $PdCl_2$. One part of the salt to 20 of water.

Potassium Chromate, K_2CrO_4. One part dissolved in 10 parts of water.

Potassium Dichromate, $K_2Cr_2O_7$. One part dissolved in 10 parts of water.

Potassium Chlorate, $KClO_3$. The crystallized salt.

Potassium Cyanide, KCy. One part dissolved in 4 parts of water.

Potassium Ferrocyanide, K_4FeCy_6. One part of the crystallized salt (3 aq.) dissolved in 12 parts of water.

Potassium Ferricyanide, K_3FeCy_6. One part dissolved in 12 parts of water.

Potassium Iodide, KI. One part dissolved in 20 parts of water.

Potassium Mercuric Iodide. Nessler's Solution. Dissolve 3.5 grams of **KI** in 10 c.c. of water; dissolve 1.6 grams of $HgCl_2$ in 30 c.c. of water; add the mercury solution gradually, and with constant stirring, to the potassium iodide solution, until the precipitate ceases to be redissolved; then add 60 c.c. Potassium hydrate solution and filter. Keep in small bottle, well stoppered.

Potassium Nitrate, KNO_3. The crystallized salt.

Potassium Metantimoniate, $KSbO_3$. (419.)

Potassium Sulphocyanate, KCyS. One part dissolved in 12 parts of water.

Potassium Hydrogen Sulphate, $KHSO_4$. (675).

Potassium Sulphate, K_2SO_4. One part dissolved in 12 parts of water.

Platinic Chloride, $PtCl_4$. One part to 10 parts of water. Also prepared by dissolving the scrap-metal in nitro-hydrochloric acid, and purifying by precipitation with ammonic chloride, dissolving again in the same acid, and evaporating to dryness.

Sodium Acetate, $Na(C_2H_3O_2)$. One part crystallized salt (3 aq.) to 5 of water.

Sodium Carbonate, Na_2CO_3. The dry salt. Also a solution of the crystals (10 aq.) in 5 parts of water.

Sodium Diborate, $Na_2O(B_2O_3)_2$. The crystallized salt (10 aq.), or dried.

Sodium Hydrate, NaOH. Solution in 9 parts of water.

Sodium Thiosulphate, $Na_2S_2O_3\ 5H_2O$. (Hyposulphite.) One part of the salt in 40 parts of water.

Sodium Hypochlorite, NaClO. Agitate one part of good bleaching-powder with ten parts of water; add solution of sodium carbonate as long as a precipitate is formed; allow the solid matter to subside and siphon off.

Sodium Phosphate, Na_2HPO_4. (Disodium hydrogen phosphate.) One part of the crystallized salt (12 aq.) in 10 parts of water.

Sodium Phosphomolybdate. (494.)

Sodium Sulphide, Na_2S. One part of the solution of soda saturated with Hydrosulphuric acid, to one part unchanged soda solution.

Sodium Sulphite, Na_2SO_3. One part of the salt to 5 parts of water.

Silver Nitrate, $AgNO_3$. One part crystallized salt in 20 parts of water.

Stannous Chloride, $SnCl_2$. One part of the crystallized salt (2 aq.) in 6 parts of water, acidulated with hydrochloric acid (429).

Strontium Sulphate, $SrSO_4$. A saturated water solution (77).

Zinc, Zn. The granulated metal.

INDEX.

PAGE

Acetates 214
Acetic Acid 214
Acid Radical 9
Acids 9
Acid Salts 10
Acids, Preliminary Examinations for 244
Acids, Tables for Determination of 244, 248
Aluminium 49
Alkalies, Precipitations by 30
Alkaline Earth Metals 37, 44
Alkali Metals 29
Ammonium 33
Analysis, Chemical, Definition of 15
Anhydride 9
Antimonic Compounds 128
Antimonious Compounds 123
" " in Oxidation 273
Antimony 123
Arsenic 112
Arsenic Compounds 120
" " in Oxidation 274
Arsenious Compounds 112
" " in Oxidation 273
Assaying 16
Atom, Definition of 15
Atomic Weights, Table of 13
Base and Acid, Definition of 9
Basic Salts 11
Bases, Grouping of 27
Bases, list, with quantivalence 11
Barium 38
Bead Reactions 225, 235
Beryllium 80
Bismuth 91
" Compounds in Oxidation 274
Blow-pipe Analysis 16, 205, 215
Bonds—as indices of Quantivalence 10
" Negative, Theory of 251
Borates 211
Boracic Acid 210

PAGE
Boron ... 210
Bromates ... 165
Bromic Acid ... 165
" " in Oxidation ... 267
Bromides ... 164
Bromine ... 163
" in Oxidation ... 266
Cadmium ... 94
Cæsium ... 36
Calcium ... 40
Carbon ... 190
Carbon, Acids of ... 190
Carbonates ... 191
Carbonic Anhydride ... 191
" " in Oxidation ... 255
Cerium ... 80
Chemical Changes. Classified ... 20
" " Causes of ... 23
" Equations ... 23
" Problems ... 24
Chemistry, Method of Analytical Study of ... 25
Chlorates ... 160
Chloric Acid ... 160
" in Oxidation ... 265
Chlorides ... 158
Chlorine ... 157
" in Oxidation ... 263
Chlorine Group of Elements ... 157
Chromic Acid ... 53
" " in Oxidation ... 275
Chromium as a Base ... 51
" " in Oxidation ... 275
Chlorochromic Acid ... 159
Citrates ... 216
Citric Acid ... 216
Classification of Metals ... 27
Cobalt ... 63
" Compounds in Oxidation ... 274
Comparison of Arsenic and Antimony Spots ... 116
Copper ... 87
" Compounds in Oxidation ... 274
Cyanates ... 188
Cyanic Acid ... 188
Cyanides ... 181
Cyanogen ... 181
Davyum ... 13
Decipium ... 13
Didymium ... 74
Dissociation, changes of ... 21
Dissolving Precipitates ... 20
Double Decomposition or Transposition ... 21

PAGE
Earths 46
Equations, Chemical 23
" in Oxidation, Examples 275
" " Rule for Writing 252
Erbium 84
Evaporation, how conducted 18
Ferric Base 54, 57
" " in Oxidation 275
Ferricyanides 186
Ferrocyanides 185
Ferrous Base 55
" " in Oxidation 275
Fifth Group Bases 29
First Group Bases 111
Flame Reactions 225
Fluorides 213
Fluorine 213
Fourth Group Bases 37, 44
Gas Analysis 15
Gallium 13
Glucinum 80
Gold 148
Group V 29, 243
" IV 37, 44, 242
" III 46, 71, 240
" II 85, 238
" I 111, 237
Grouping of the Bases 27
Hydracids 9
Hydrates 10
Hydriodic Acid 167
" " in Oxidation 268
Hydrobromic Acid 163
" " in Oxidation 267
Hydrochloric Acid 158
" " in Oxidation 264
Hydrocyanic Acid 181
" " in Oxidation 269
Hydroferricyanic Acid 186
" " in Oxidation 270
Hydroferrocyanic Acid 184
" " in Oxidation 270
Hydrofluoric Acid 213
Hydrofluosilicic Acid 214
Hydrosulphuric Acid 195
" " in Oxidation 259
Hydroxide, defined 11
Hypochlorites 162
Hypochlorous Acid 162
" " in Oxidation 265
Hypophosphorous Acid 210

PAGE
Hyposulphurous Acid ... 203
Indium ... 84
Ilmenium ... 13
Iodates ... 171
Iodic Acid ... 170
" " in Oxidation ... 269
Iodides ... 168
Iodine ... 166
" in Oxidation ... 268
Iridium ... 156
Iron ... 54
Lanthanum ... 84
Lavoisium ... 13
Lead ... 95
" Oxide in Oxidation ... 270
" Peroxide in Oxidation ... 271
Liquid State, How Produced ... 17
Lithium ... 35
Magnesium ... 42
" Separation of, from Fourth Group ... 45
" " from Fifth Group ... 46
Manganates ... 60
Manganese ... 60
" Peroxide in Oxidation ... 274
Manganous Compounds, in Oxidation ... 274
Metals as Bases, Classification of ... 27
Metaphosphates ... 208
Mercuric Salts ... 107
" " in Oxidation ... 272
Mercurous Salts ... 105
" " in Oxidation ... 272
Mercury ... 104
Metals, separated ... 201
Methods of Analysis ... 16
Molecules ... 15
Molybdic Acid ... 153
Molybdenum ... 153
Monobasic Acids ... 9
Mosandrum ... 13
Neptunium ... 13
Nickel ... 66
" Compounds in Oxidation ... 274
Niobium ... 84
Nitrates ... 177
Nitric Acid ... 176
" " in Oxidation ... 256
Nitric Anhydride ... 176
Nitrites ... 180
Nitrogen ... 175
" Group of Elements ... 175
Nitro-hydrochloric Acid ... 159

PAGE
Nitrous Acid ... 180
" " in Oxidation ... 255
Normal Salts ... 10
Notation of Metallic Compounds ... 9
Order of Study ... 26
Organic Analysis, Ultimate and Proximate ... 15
Organic Substances, Removal of ... 220
Osmium ... 156
Oxacids ... 9
Oxalates ... 193
Oxalic Acid ... 193
" " in Oxidation ... 253
Oxidation and Reduction ... 250
Antimony ... 273
Arsenic ... 273
Bromic Acid ... 267
Bromine ... 266
Carbonic Acid ... 255
Chloric Acid ... 265
Chlorine ... 263
Cobalt ... 274
Copper ... 274
Chromium ... 275
Hydrocyanic Acid ... 269
Hydroferrocyanic Acid ... 270
Hydroferricyanic Acid ... 270
Hydriodic Acid ... 268
Hydrochloric Acid ... 264
Hydrosulphuric Acid ... 259
Hypochlorous Acid ... 265
Hypophosphorous Acid ... 258
Iodic Acid ... 269
Iodine ... 268
Iron ... 275
Lead ... 270
Manganese ... 274
Mercury ... 272
Nickel ... 274
Nitric Acid ... 256
Nitrous Acid ... 255
Oxalic Acid ... 253
Phosphoric Acid ... 259
Silver ... 271
Sulphuric Acid ... 262
Sulphurous Acid ... 261
Tin ... 272
Oxidation and Reduction, Changes of ... 21, 251
Oxides ... 10
Perchloric Acid ... 161
Palladium ... 152
Permanganates ... 60

PAGE
Permanganates in Oxidation 274
Periodic Acid 167
Philipium 13
Phosphoric Acid 205
" " in Oxidation 259
Phosphorus 205
Plan for Third Group Separations by Carbonate of Barium 79
" Treating Phosphates in the Third Group 78, 241
" Separation by Ammonia and Chloride of Ammonium 72
" Separation by Alkalies in the Third Group 76
Plan of Work 26
Platinum 149
Potassium 31
Precipitation, Defined 17
Preliminary Examinations 17, 222, 227
Problems in Parts by Weight 24
Pseudo-triads 11
Pyrophosphates 208
Qualitative Analysis, Defined 15
Quantivalence 10
Radical, Defined 9
Reagents, How used 18
" List of 296
Rhodium 156
Rubidium 36
Ruthenium 156
Salts 9
Saturation by Acids, etc 20
Second Group Bases 85
Selenium 156
Separation of Fifth Group Metals 46
" of Fourth Group Metals 45
" of Third Group Metals 75
" of First and Second Group Metals 136
" of the Bases without the use of hydrosulphuric acid 145
" of Acids of Chlorine, etc 174
" of Acids of Sulphur 204
Silicic Acid 212
Silicon 212
Silver 100
" Compounds in Oxidation 271
Sodium 32
Solubilities of Metallic Salts, Lists of, With each Base 284
" " " " With each Acid 292
Solution, Defined 17
Spectral Analysis 17
Stannic compounds 133
Stannous compounds 131
Strontium 40
Sulphocyanates 188
Sulphocyanic Acid 188

PAGE
Sulphocyanic Acid in Oxidation 269
Sulphosalts 112
Sulphur 194
" Acids of 195
Sulphates 197
Sulphides 195
Sulphites 199
" in Oxidation 261
Sulphuric Acid 197
" " in Oxidation 262
Table of Atomic Weights 13
Tantalum 84
Tartaric Acid 215
Tartrates 215
Tellurium 156
Thiosulphate Process 74
Thiosulphuric Acid 188
Third Group of Bases 46, 71
Thorium 84
Transposition, changes of 21
Tungsten 156
Thallium 82
Tin 130
" Compounds in Oxidation 272
Titanium 81
Uranium 81
Vanadium 84
Washing Precipitates 19
Yttrium 84
Zinc 68
Zirconium 84

SCIENTIFIC BOOKS

PUBLISHED BY

D. VAN NOSTRAND,

23 Murray Street and 27 Warren Street,

NEW YORK.

Any Book in this Catalogue, sent free by mail on receipt of price.

Weisbach's Mechanics.

Fourth Edition, Revised. 8vo. Cloth. $10.00.

A MANUAL OF THEORETICAL MECHANICS. By Julius Weisbach, Ph. D. Translated from the fourth augmented and improved German edition, with an introduction to the Calculus, by Eckley B. Coxe, A. M., Mining Engineer. 1100 pages and 902 wood-cut illustrations.

Francis' Lowell Hydraulics.

Third Edition. 4to. Cloth. $15.00.

LOWELL HYDRAULIC EXPERIMENTS—being a Selection from Experiments on Hydraulic Motors, on the Flow of Water over Weirs, and in open Canals of Uniform Rectangular Section, made at Lowell, Mass. By J. B. Francis, Civil Engineer. Third edition, revised and enlarged, including many New Experiments on Gauging Water in Open Canals, and on the Flow through Submerged Orifices and Diverging Tubes. With 23 copperplates, beautifully engraved, and about 100 new pages of text.

Kirkwood on Filtration.

4to. Cloth. $15.00.

REPORT ON THE FILTRATION OF RIVER WATERS, for the Supply of Cities, as practised in Europe, made to the Board of Water Commissioners of the City of St. Louis. By JAMES P. KIRKWOOD. Illustrated by 30 double-plate engravings.

Pynchon's Chemical Physics.

New Edition. Revised and enlarged. Crown 8vo. Cloth. $3.00.

INTRODUCTION TO CHEMICAL PHYSICS; Designed for the Use of Academies, Colleges, and High Schools. Illustrated with numerous engravings, and containing copious experiments, with directions for preparing them. By THOMAS RUGGLES PYNCHON, M.A., President of Trinity College, Hartford.

Eliot and Storer's Qualitative Chemical Analysis.

New Edition. Revised. 12mo. Illustrated. Cloth. $1.50.

A COMPENDIOUS MANUAL OF QUALITATIVE CHEMICAL ANALYSIS. By CHARLES W. ELIOT and FRANK H. STORER. Revised, with the coöperation of the Authors, by WILLIAM RIPLEY NICHOLS, Professor of Chemistry in the Massachusetts Institute of Technology.

Rammelsberg's Chemical Analysis.

8vo. Cloth. $2.25.

GUIDE TO A COURSE OF QUANTITATIVE CHEMICAL ANALYSIS, ESPECIALLY OF MINERALS AND FURNACE PRODUCTS. Illustrated by Examples. By C. F. RAMMELSBERG. Translated by J. TOWLER, M.D.

Naquet's Legal Chemistry.

Illustrated. 12mo. Cloth. $2.00.

LEGAL CHEMISTRY. A Guide to the Detection of Poisons, Falsification of Writings, Adulteration of Alimentary and Pharmaceutical Substances; Analysis of Ashes, and Examination of Hair, Coins, Fire-arms, and Stains, as Applied to Chemical Jurisprudence. For the Use of Chemists, Physicians, Lawyers, Pharmacists, and Experts. Translated, with additions, including a List of Books and Memoirs on Toxicology, etc., from the French of A. NAQUET. By J. P. BATTERSHALL, Ph. D., with a Preface by C. F. CHANDLER, Ph. D., M.D., LL.D.

Prescott's Qualitative Chemistry.

12mo. Cloth. $1.50.

FIRST BOOK IN QUALITATIVE CHEMISTRY. By ALBERT B. PRESCOTT, Professor of Organic and Applied Chemistry in the University of Michigan.

Prescott's Proximate Organic Analysis.

12mo. Cloth. $1.75.

OUTLINES OF PROXIMATE ORGANIC ANALYSIS, for the Identification, Separation, and Quantitative Determination of the more commonly occurring Organic Compounds. By ALBERT B. PRESCOTT, Professor of Organic and Applied Chemistry in the University of Michigan.

Prescott's Alcoholic Liquors.

12mo. Cloth. $1.50.

CHEMICAL EXAMINATION OF ALCOHOLIC LIQUORS.—A Manual of the Constituents of the Distilled Spirits and Fermented Liquors of Commerce, and their Qualitative and Quantitative Determinations. By ALBERT B. PRESCOTT, Professor of Organic and Applied Chemistry in the University of Michigan.

Prescott and Douglas's Qualitative Chemical Analysis.

Third Edition. Revised. 8vo. Cloth. $3.50.

A Guide in the Practical Study of Chemistry and in the Work of Analysis.

Mott's Chemists' Manual.

8vo. 650 pages. Cloth. $6.00.

A PRACTICAL TREATISE ON CHEMISTRY (Qualitative and Quantitative Analysis), Stoichiometry, Blowpipe Analysis, Mineralogy, Assaying, Pharmaceutical Preparations, Human Secretions, Specific Gravities, Weights and Measures, etc., etc., etc. By HENRY A. MOTT, JR., E. M., Ph. D.

Beilstein's Chemical Analysis.

12mo. Cloth. 75c.

AN INTRODUCTION TO QUALITATIVE CHEMICAL ANALYSIS. By F. BEILSTEIN. Third edition, translated by I. J. OSBUN.

Caldwell & Breneman's Chemical Practice.

8vo. Cloth. 188 pages. Illustrated. New and Enlarged edition. $1.50.

MANUAL OF INTRODUCTORY CHEMICAL PRACTICE, for the use of Students in Colleges and Normal and High Schools. By Prof. GEO. C. CALDWELL and A. A. BRENEMAN, of Cornell University. Second edition, revised and corrected.

Joynson on Machine Gearing.

8vo. Cloth. $2.00.

THE MECHANIC'S AND STUDENT'S GUIDE in the designing and Construction of General Machine Gearing, as Eccentrics, Screws, Toothed Wheels, etc., and the Drawing of Rectilineal and Curved Surfaces. Edited by FRANCIS H. JOYNSON. With 18 folded plates.

Maxwell's Matter and Motion.

16mo. Boards. 216 pages. 50c.

MATTER AND MOTION. By Prof. J. CLARK MAXWELL.

Barnes' Submarine Warfare.

8vo. Cloth. $5.00.

SUBMARINE WARFARE, DEFENSIVE AND OFFENSIVE. Descriptions of the various forms of Torpedoes, Submarine Batteries and Torpedo Boats actually used in War. Methods of Ignition by Machinery, Contact Fuzes, and Electricity, and a full account of experiments made to determine the Explosive Force of Gunpowder under Water. Also a discussion of the Offensive Torpedo system, its effect upon Iron-clad Ship systems, and influence upon future Naval Wars. By Lieut.-Com. JOHN S. BARNES, U.S.N. With twenty lithographic plates and many wood-cuts.

Foster's Submarine Blasting.

4to. Cloth. $3.50.

SUBMARINE BLASTING, in Boston Harbor, Massachusetts—Removal of Tower and Corwin Rocks. By JOHN G. FOSTER, U. S. Eng. and Bvt. Major-General U. S. Army. With seven plates.

Plympton's Aneroid Barometer.

16mo. Boards, illustrated, 50c. Morocco, $1.00.

THE ANEROID BAROMETER: Its Construction and Use, compiled from several sources.

Williamson on the Barometer.

4to. Cloth. $15.00.

ON THE USE OF THE BAROMETER ON SURVEYS AND RECONNAISSANCES. Part I.—Meteorology in its Connection with Hypsometry. Part II.—Barometric Hypsometry. By R. S. WILLIAMSON, Bvt. Lt.-Col. U. S. A., Major Corps of Engineers. With illustrative tables and engravings.

3 1197 00467 2116